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NATIONAL DEFENSE RESEARCH COMMITTEE

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OFFICE OF SCIENTIFIC RESEARCH AND DEVELOPMENT

First Report on "Rheological Properties of Thickened Liquids"

June, 5, 1942  
to  
December 1, 1942

by

E. K. Carver and G. Broughton

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First Report on "Rheological Properties of Thickened Liquids"  
(CWS-10, 12, 21; NL-B36)

Endorsement (1) From T. K. Sherwood, Chairman, Section B-8  
to Roger Adams, Chairman, Division B. Forwarding report and  
noting:

"In the course of the development of liquid chargings and other liquid dispersing devices by the armed services, it has been found that too rapid a breakup of the liquid mass is, in many cases a distinct disadvantage. The use of various thickening materials added to liquids has been found to overcome partially too rapid a breakup. However, thickened fluids differ in rheological properties from ordinary fluids, the viscosity of which is independent of the rate of shear. The present work was designed to define and measure these differences in an attempt to account for the better performance of thickened fluids in practice.

"The thickened fluids investigated are of two main types, first, solutions of a basic aluminum soap in gasoline, and second, methacrylate copolymers also dissolved in gasoline, with or without the addition of a soap such as sodium stearate.

"For the above work it has been necessary to design and construct suitable devices and apparatus for the measurement of the properties desired. These include such devices as a viscosimeter constructed from the bed of a jeweler's lathe, a viscosimeter constructed to subject the fluid to an oscillational force, a high pressure jet to subject the fluids to treatment analogous to that which they would receive under the conditions of actual use in a flame thrower or other device where they are ejected from a small orifice under high pressure, a device to obtain a measurement of the "stringiness" shown by a fluid. In addition to the original instruments devised,

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viscosimeters of many well-known types such as the Clark-Hodsmann, MacMichail, etc. have been employed. As these latter types are more or less standard equipment, the details of their construction and use is left largely to references. However, sufficient detail of the apparatus original to this work is contained in the report to enable other workers to duplicate and use these devices.

"The theoretical considerations of thickened fluids which have been developed in this report have been applied in the main to study of a breakup of unignited jets and the ejection of the incendiary material as applicable to the M56 incendiary bomb (now known as the M69 bomb). In addition to the continuation of work along these lines, it is expected that in the near future the theoretical considerations involved will be applied to the thickening of vesicants."

(2) Twenty-eight copies forwarded to Dr. Irvin Stewart, Secretary of the National Defense Research Committee, as Progress Report under Contract B-300, OEMsr-538 with Eastman Kodak Co.

Roger Adams, Chairman  
by Harris M. Chadwell  
Technical Aide

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## S U M M A R Y

Thickened fluids are being used as fuel in flame throwers and in the incendiary bomb. They differ in rheological properties from ordinary fluids, the viscosity of which is independent of rate of shear.

The present work was designed to define and measure these differences in an attempt to account for the better performance of thickened fluids in practice.

The thickened fluids investigated are of two main types, X-104\* dissolved in gasoline and isobutyl methacrylate copolymerized with a small amount of methacrylic acid and dissolved in gasoline with or without the addition of soaps such as sodium stearate. Such fluids are all found to be pseudoplastic, possessing a consistency curve similar to that of Fig. 1(b). They may or may not be thixotropic, have a yield value or show work-hardening. The isobutyl methacrylate interpolymers show considerable fore- and after-elastic effects and all show measurable rigidity. Measurements of rigidity made by oscillational methods show it to be independent of frequency and indicate no unusual short time effects which might become important under the conditions encountered in practical use. Rheological properties of the typical thickened fluids are summarized in Fig. 5 and Table V.

Unignited  $1/8$  inch jet experiments were made in an attempt to correlate performance of thickened fluids in the flame thrower with their measured rheological properties. No significant correlation was observed between range and any variable except the apparent viscosity of the thickened fluid. Fig. 34 shows a semi-log plot of apparent viscosity at a rate of shear of 30 reciprocal seconds versus range for a number of fluids compared at the same initial nozzle kinetic energy. Falling on the same line are Newtonian, pseudoplastic (with and without a yield value), thixotropic and dilatant fluids covering a viscosity range from 0.1 to 8000 poises. The only deviations are shown by liquids of low viscosity and high surface tension. This leads to the belief that the prime requirement for a flame thrower thickened fluid is pseudoplasticity, i. e., the possession of low apparent viscosity at high rates of shear, which allows easy passage through the orifice with consequent attainment of high initial jet kinetic energies, and high apparent viscosity at low rates of shear, which prevents break-up of the stream by the drag of the surrounding air (diagram p. 28). Nevertheless, this is not the complete story, since certain liquids, which are "short", i. e., lack stringiness, and which also have high moduli of rigidity, do not follow this rule. Other factors may also have some influence. It appears

\*A basic aluminum soap of oleic, naphthenic and coconut oil fatty acids.

correct to state, therefore, that pseudoplasticity is a requirement for high range in the flame thrower but does not necessarily guarantee good performance.

In the incendiary bomb (M56) the requirements seem to be similar to those of the flame thrower. The filling must be expelled from the casing, requiring low apparent viscosity at the high rate of shear involved, and must then travel through the air to the target without break-up, requiring high apparent viscosity at a somewhat low rate of shear. The limited preliminary experimental results seem to bear out this viewpoint, although complicating effects due to the explosion may be present. Another important factor in incendiary bomb performance is adhesion to the target. Little is known of the variables controlling this. It appears certain that the following requirements must be met:

1. It must be soft enough so that the impact of the mass upon the wall will flatten it out into a firm, thin layer without too much fracture.

2. It must have a yield value or at least a high-enough apparent viscosity at low rates of shear so that the mass after being flattened out on the wall will not run off too rapidly.

3. It must have a little stringiness. This should be low enough so that it will not bounce off the wall and preferably low enough so that the flattened mass will not draw together again after being flattened and fall off. The exact rheological properties required to produce the above qualities have not yet been entirely determined.

## FIRST REPORT

on

### RHEOLOGICAL PROPERTIES OF THICKENED FLUIDS.

October 14, 1942

#### Introduction:

In May, 1942, this group was asked, under N.D.R.C. Contract OEMsr-538, to investigate the rheological properties of thickened fluids, the use of which has been found advantageous in three weapons of war, namely:

1. Incendiary bombs,
2. Flame throwers,
3. Vesicants.

In incendiary bombs the use of thickened gasoline rather than gasoline itself avoids the atomization and flash-burn encountered with the latter and a hot steady flame lasting a considerable time (4 to 6 minutes with the 8 pound M-56 bomb) is obtained. Greatly increased ranges result with the use of thickened fluids in the flame thrower, the range of the service portable flame thrower using a 5/16 in. nozzle and 150 pound pressure being increased from approximately 35 to 70 yards when a given thickened gasoline is substituted for gasoline or fuel oil. Little has been done with vesicant thickening agents.

The thickening agents employed for incendiary bombs and flame throwers have been principally aluminum or sodium soaps and isobutyl methacrylate polymers. These materials when suitably dispersed in gasoline give rise to colloidal gels or solutions which show marked departures from the normal rheological properties of a liquid. Thus, their flow characteristics are non-Newtonian and many of them possess measurable rigidity. The question arose as to which of these unusual physical properties were responsible for the increased efficiency of the thickened fluids in bombs and flame throwers. If it were possible to identify these and then to predict from their laboratory measurement actual ranges in the flame thrower or actual bomb performance, this would allow easy testing of any materials suggested as thickeners. Furthermore, the search for new and better thickeners should be stimulated.

During the past few months measurements of the apparent viscosity, modulus of rigidity, work hardening, thixotropy and other properties of a large number of thickened fluids have



been made using a variety of instruments. Measurements have been made with the normal viscosimetric techniques, at frequencies of from 5 to 600 cycles per second and under suddenly imposed shock. Simultaneously, a limited number of practical tests have been made. For unignited flame thrower studies a 1/8 inch 37° conical nozzle similar to that used by Hottel and Garraway\* was installed. By the courtesy of the Bayway group a number of M-56 bombs were filled with widely varying liquids and the results on static ignition studied. Consideration of the results obtained in these tests has led to a point of view which, while it undoubtedly does not express the complete picture, is believed to formulate at least partially the essential requirements for a thickened fluid.

## P A R T I

### Rheological Properties.

Since it will be necessary to use many terms such as pseudoplasticity, work-hardening, etc., a short discussion of rheological properties, defining the terminology used may be in order.

For normal liquids the stress (F)-rate of shear (dV/dr) curve is a straight line (Figure 1(a)), the slope of which gives the reciprocal of the viscosity ( $\eta$ ).

$$dV/dr = 1/\eta F \quad (1)$$

Many colloidal solutions and dispersions, e.g. rubber in toluene, show curves of the type of Figure 1(b) - pseudoplasticity. In many cases, such curves may be expressed by the equation

$$dV/dr = 1/\eta F^n \quad (2)$$

Pastes and suspensions, e.g. paint, clay in water, frequently show so-called Bingham plasticity (Fig. 1(c)) which follows the equation:

$$dV/dr = 1/\eta (F-f) \quad (3)$$

where f is the intercept on the stress axis, the so-called yield value. The precise shape of the curve at the lower rates of shear is debatable; it may curve in to the origin in many cases.

Still another type of curve (Fig. 1(d)) is shown by other pastes, where the apparent viscosity increases with increasing shearing force. Such a system is said to show dilatancy.

\*"Joint Report on Status of N.D.R.C. Projects on Flame Throwers" 6.24.42.

Frequently, the consistency curve of a system changes when it is allowed to stand undisturbed. Most of the curve types shown in Fig. 1 can be obtained with the shape of the curve also dependent upon the past history of the sample. Hence, in many systems, time must be considered as a third variable. If the apparent viscosity tends to increase with time of undisturbed standing at constant temperature, the system is said to be thixotropic.

Upon imposition of a stress, flow is complete for the systems discussed thus far. When the stress is removed, there is no recovery of the specimen toward its former condition. If upon removal of the stress there should be some recovery, then we have a visco-elastic material. Fig. 1(e) shows a plot of velocity gradient versus time after application of a constant stress. When the deforming force is removed, there is a slow partial recovery of the deformation. Such a liquid is said to show fore- and after-elastic effects.

According to Maxwell\* the properties of a material intermediate between a liquid and a solid can be treated in the following manner. In a body free from viscosity, i.e., having the characteristics of a solid only,

$$F = ES$$

where E is the modulus of elasticity and S is the deformation. Further, if t is the time

$$dF/dt = E \cdot dS/dt$$

If, however, the material is viscous, some flow will occur and the stress F will tend to disappear. The simplest assumption is that it will disappear at a rate proportional to F.

$$dF/dt = E \cdot dS/dt - F/T \quad (5)$$

When the deformation S is constant, dS/dt is zero and

$$T = F/dF/dt \quad (6)$$

T is known as the relaxation time. It is the time taken for the stress to decrease to 1/e of its original value. For liquids it is extremely small, for perfect solids infinite.

\*Maxwell, Phil. Mag. (4) 35, 133, 1868

A complete classification of the behavior of non-gaseous bodies upon deformation was recently given in "Nature"\*, and this will be adhered to as far as possible in the following discussion:

Properties of Thickened Fluids of Possible Importance in the  
Flame Thrower and Incendiary Bomb.

For a normal, Newtonian fluid physical properties which might play a part in performance would seem to be limited to:

1. Viscosity,
2. Density,
3. Surface Tension,

These have been investigated by Hottel and Garraway (loc. cit.) for unignited jets in the flame thrower, who concluded "viscosity is moderately important and surface tension quite important in determining the range expected from a fluid". No investigation of simple, Newtonian fluids appears to have been made in the case of the incendiary. However, in Porton Report No. 2215, the fragmentation of liquid chemical warfare agents is discussed and several interesting experiments on bursting bombs described. These included the following:

- A. High speed cinematography shows a fine spray of the liquid at the moment of ejection.
- B. When a tail-ejection type bomb is functioned, the large droplets of liquid are found nearest the bomb, the finest furthest away but none more than 20 yards away.
- C. If the steel end plate of the bomb is replaced by a rubber diaphragm much coarser fragmentation is obtained.
- D. A bomb was filled with three miscible layers of liquids of different density and colored with different dyes. The large drops near the bomb were all produced by the lowest layer nearest the bursting charge. Very few drops showed any signs of mixing of the layers.

It was concluded that oscillation was largely responsible for fragmentation and that increase in viscosity should reduce the latter.

With the incorporation of gums or high molecular weight polymers in gasoline, enormous changes in viscosity become

\*Nature, 149, 702, 1942

possible, while density and surface tension are hardly affected. At the same time a number of new physical properties make their appearance; the thickened fluids are no longer Newtonian but as a general rule appear to be visco-elastic. Hence, as other factors possibly dictating practical performance we must consider:

4. Extent and character of departure from Newtonianism,
5. Presence or absence of a yield-value,
6. Modulus of rigidity,
7. Relaxation time,
8. Thixotropy,
9. Work hardening,

Time effects may be of particular importance. Thus, for the flame thrower, a thixotropic liquid with a high rate of recovery would seem to be ideal. On passage through the nozzle the structure would be broken down but a high rate of set would allow it to rebuild rapidly to resist break-up of the liquid jet by the air. For this reason attention was paid to measurements of modulus of rigidity and viscosity at short time intervals after stress was applied. In the incendiary bomb thixotropy with slow accommodation may be of importance. The bombs will undoubtedly stand for long periods before firing, allowing the maximum amount of structure to be built up, which might reduce considerably the break-up of the filling during explosion.

It was felt necessary to investigate all the above properties for typical thickened fluids, at least in a preliminary manner, and for this reason a number of different types of viscosimeters have been used. It must be remembered that the solutions used are none too reproducible and hence the values given in this report are good only for the particular samples measured and are only indicative of those for their class. In the case of X-104 solutions, the rheological properties appear to be greatly influenced by the water content of the solid soap.

#### Rheological Measurements.

Ordinary viscosity measurements have been made principally upon four instruments, the Clark-Hodgman, the MacMichael, the Stormer and the high pressure capillary viscosimeter. Recently a Gardner Mobilometer has also been obtained.



The Clark-Hodgman viscosimeter\* (Fig. 2) is a torsion viscosimeter which may be used for the determination of viscosities at low rates of shear, of the order of 0.01 to 1.0 seconds<sup>-1</sup>, and also for the determination of elasticities and relaxation times. It consists of a cylinder, 2.3 cms. diameter, suspended by a torsion wire inside an outer cylinder of 2.58 cms. internal diameter. The deflection of the inner cylinder is measured by an attached pointer and a scale graduated in degrees. The torque applied is similarly measured at the top of the torsion wire by another pointer and scale. By twisting the torsion wire through, say 90 degrees, and timing the travel of the lower pointer until equilibrium is reached, a shearing force-deformation curve can be obtained and thence a normal consistency curve, velocity gradient-shearing force. The instrument can be calibrated using a Bureau of Standards oil of known viscosity or its constants may be calculated from the dimensions. Good agreement is obtained between the two methods.

The MacMichael viscosimeter\*\* consists of an inner cylinder suspended by a torsion wire inside an outer cup which can be rotated by an electrical motor at from 5 to 50 r.p.m. Measurements are made of the torque and the r. p. m. and from these an apparent viscosity versus rate of shear curve can be obtained, calibration again being made with the aid of a standard oil. The MacMichael covers a rate of shear range of approximately from 3 to 100 seconds<sup>-1</sup>.

To obtain velocity gradients ranging from about 1000 to 100,000 seconds<sup>-1</sup> the high pressure capillary viscosimeter (Fig. 3) has been employed. The liquid under test is charged into a cylinder at the bottom of which is inserted a capillary of known length and radius. The liquid is forced out through this capillary by a constant known nitrogen pressure. The constants of the instrument can again be determined by calibration with a liquid of known viscosity or calculated from the dimensions of the apparatus.

The Stormer\*\*\* viscosimeter has been used principally for specification work and for following the course of aging experiments. A paddle is rotated by means of a falling weight inside a cup containing the liquid (for dimensions of the parts see Fig. 4). In this form the instrument suffers from the

\* J. Soc. Chem. Ind. 56, 67, 1937

\*\* For a full description see Barr "A Monograph of Viscometry" Oxford U. Press, 1931, p. 219

\*\*\* For a full description see Barr "A Monograph of Viscometry" Oxford U. Press, 1931, p. 235

defect that rate of shear cannot be calculated in absolute units. It appears from the results obtained that it lies somewhat below that given by the MacMichael viscosimeter.

Fig. 5 shows typical viscosity data obtained on the above instruments for most of the thickened fluids suggested for practical use\* and for a number of liquids which have been used to test out the theories outlined below. While the curves for the different instruments do not overlap as well as might be desired, the general trend is obvious. The discrepancies may be fundamental but more probably are due to end-effects, inaccuracies in calibration, etc.

In general, the viscosities of X-104 thickened gasolines appear to increase with temperature, there being a minimum in the viscosity-temperature curve as measured on the MacMichael at about 70°F.

#### Viscosity Changes Under Sudden Stress

The viscosities shown in Fig. 5 and measured as described above are essentially dynamic or equilibrium values. They are obtained, with the exception of the Clark-Hodgman, after the liquid has undergone extensive shear and give no information as to the behavior which might be expected when a sudden shearing stress is applied. The latter must occur in the tail-ejection type of incendiary bomb when the filling is pushed out by the explosion gases. An attempt to obtain data of this type has been made with the so-called jeweler's lathe viscosimeter.

The instrument (Fig. 6) is a rotating-cylinder type viscosimeter with three modifications. First, the outer cup, A, can be made to rotate instantaneously at speeds from 20 to 1080 r.p.m. by means of a gear train, B, and clutch. Thus, the synchronous electric motor, C, may be started to run, movement of a lever then causes the outer cylinder, A, to rotate instantaneously. Second, the inner cylinder is suspended from the tailstock of the jeweler's lathe by a torsion rod, E, 0.206 cm. in diameter, so that movement of the inner cylinder even with the most viscous materials is almost negligible. The necessary accuracy in reading the deflection is obtained by attaching a mirror, F, to the torsion rod, a trace on 35 mm. cine film, driven by a synchronous motor at 18.7 cm. per sec., being obtained. Third, to obtain quick response the inner cylinder is hollow\*\* and the period of vibration

\* Formulae for these are given in Appendix I.

\*\* To avoid buoyancy it is filled with chloroform.

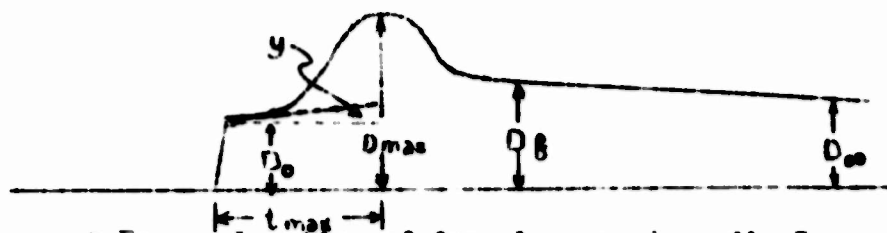
of the inner cylinder-torsion rod system is only 0.011 seconds. minor features are the lower bearing, which was found essential to prevent the inner cylinder from being dragged from its central position, the cover (G) on top of the outer cylinder which was necessary to keep the material from crawling up the torsion rod and a thermostatic cup, H, placed around the outer cylinder.

The material under investigation is placed in the cup and allowed to stand for several hours to remove any air bubbles. Rotation may then be started and the deflection of the inner cylinder followed visually on a scale or photographically. Fig. 7 shows typical photographic traces for:

1. Bureau of Standards calibration oil,  
Viscosity 13.35 poises. Newtonian liquid.
2. 40% butyl methacrylate in gasoline.  
Viscosity 150 poises. Newtonian liquid.
3. 8% Bentonite in water. Thixotropic.
4. Starch-glucose-glycerine mixture. Dilatant.
5. Formula 241\*.
6. Formula 2600.
7. 9% X-104
8. 3A1-1.

The distance of the camera from the mirror is noted in the lower left hand corner of each trace.

Below is a schematic tracing, showing the quantities it has been possible to measure in order to characterize the tracings obtained. These are



\* For explanation of formula, see Appendix I.

$D_0$  = the deflection of the torsion rod, which appears at the same rate as would the deflection corresponding to Newtonian viscosity.  $D_{max}$  = the maximum deflection.  $D_f$  = the deflection obtained after  $D_{max}$  has been passed; it may or may not decrease with time to:  $D_e$  = the final equilibrium deflection for a given rate of shear.  $t_{max}$  = the time from the start of rotation to reach  $D_{max}$ .  $Y$  = the angle at which the rise to  $D_{max}$  begins.

Table I shows schematically the behavior with respect to these quantities of the various classes of materials examined.

**TABLE I**  
**BEHAVIOR ON THE JEWELER'S LATHE VISCOSIMETER.**

<u>Materials.</u>	<u>Rate of</u> <u>Shear.</u>	<u><math>D_0</math></u>	<u><math>D_{max}</math></u>	<u><math>D_f</math></u>	<u><math>D_e</math></u>	<u><math>Y</math></u>	<u><math>t_{max}</math></u>
Newtonian	All	$D_0 = D_{max} = D_f = D_e$				0	0
Bentonite ) Formula 241 ) A-2600* )	low	$D_0 < D_{max} \approx D_f > D_e$ measurable				0	0
	high	$D_0 \approx D_{max} \approx D_f > D_e$				0	0
X-104 ) Isobutyl methacry- ) late interpolymers ) X-104 + pulped ) newsprint ) X-104 + Polypalc ) resin )		$D_0 < D_e$ ; $D_{max} > D_f = D_e$ measurable					.14-.65 sec
		$D_{max}$ is a function of rest time.					.29-3.2 "
		$D_{max}$ increases with increasing rate of shear.					
		$D_e$ increases with increasing rate of shear.					.05-.24 "
						For X-104, $Y$ increases with increasing rate of shear.	
						* For A-2600 $D_{max}$ may be $> D_e$ . For 3A1-3, $Y$ decreases with increasing rate of shear.	

The traces for Newtonian fluids show a sudden, sharp rise at the moment the outer cylinder starts to rotate followed by a constant deflection, proportional to the viscosity of the fluid. Small variations in the trace should be neglected, as they have been proved due to instrument vibrations. The rate at which the equilibrium deflection is reached is exactly the same which would result if the inner and outer cylinder were connected mechanically and the outer cylinder rotated. This indicates that for true liquids equilibrium conditions of flow are reached in a time that is immeasurable on this apparatus.



Very different traces are given by X-104 and isobutyl methacrylate interpolmer thickened gums, a pronounced  $D_{max}$ , which is a function of the time the solution is allowed to stand undisturbed in the cup between runs (Figs. 8\* and 9\*), being obtained. Calling this time the rest time, it can be seen that the X-104 thickened liquids show a much more rapid build-up of  $D_{max}$  with rest time than the isobutyl methacrylate interpolymers. In Figs. 10 and 11,  $D_{max}$  is plotted vs. rest time for the two types of thickening agents. The curves tend to an asymptote for  $D_{max}$ , its value being  $D_{max}^{\infty}$  for infinite rest time.

When  $(D_{max}^{\infty} - D_{max})$ , i.e. the difference between the deflection and the maximum deflection, is plotted against rest time,  $t$ , on semi-log paper (Fig. 12) a straight line is obtained for the X-104 thickened materials indicating that:

$$\frac{d(D_{max}^{\infty} - D_{max})}{dt} = -k(D_{max}^{\infty} - D_{max})$$

This might be expected if the change occurring were from one simple statistical distribution to another. As seen for 9% X-104, the lines for different rates of shear are all parallel, indicating the same rate constant. For the isobutyl methacrylate interpolmer thickened materials there appears to be no simple logarithmic relationship.

For X-104 solutions the rest time necessary to reach  $D_{max}^{\infty}$  is greatly increased at low temperatures and decreases at high, straight lines of the type of Fig. 12 still resulting when the data are plotted in the same manner. From the values it may be calculated that the activation energy of the change occurring is 8.9 kilogram-calories, which is quite close to that of the hydrogen linkage (about 8.5 kilogram-calories).

Figure 13 shows a log-log plot of apparent viscosity,  $\eta_a$ , calculated from the values of  $D_a$  vs. velocity gradient for 9% X-104 at different rates of shear and temperatures. It will be seen that the points lie on a single straight line. Comparison of the data with that of Fig. 5 shows that the line lies parallel to that measured on the MacMichael for 9% X-104, although the absolute values of the apparent viscosity are low, forming more nearly a continuation of the Clark-Hodgman line for 9% X-104. Also shown on Fig. 13 are the points for  $\eta_{max}$ , calculated from  $D_{max}$ . Here the points do not lie on a straight line and  $\eta_{max}$  increases with temperature.

The interpretation of the above results obtained on the "jeweler's" or the viscosimeter is not altogether clear. Pseudoplastic liquids divide themselves into two classes, those which give the characteristic hump in the deflection curve and those which do not. This corresponds to the difference in appearance

\* Note that in these figures the trace is reversed, the start of the experiment being on the right hand side of the figure.

of the two types. The former, examined under the microscope, are either optically clear (X-104) or show relatively large spherules of water (isobutyl methacrylate interpolymers). The latter are definitely opaque. Formula 241 shows a large number of very small water globules under the microscope, approximately one fortieth of the size of those observed in the interpolymers. The latter type, while they have a high rigidity on the Clark-Hodgman (vide infra), show little elastic after-recovery, differing markedly in this respect from the isobutyl methacrylate interpolymers. In the former type it may be suspected that their high viscosity is due to the mutual interference of long chain molecules, which form a weakly bonded structure when undisturbed\*. On subjection to sudden shear, the tangled snarl of fibrillae tends to straighten and as extension occurs the bonds are strained and finally break. After a rest period, they have reformed, at least partially, and the process can be repeated. In the latter type, high viscosity may be due to interference between the spherules which are mutually independent units. While there may be some preferred groupings, broken down on prolonged shear, thus accounting for the observed thixotropic effect, these will not give any maximum on sudden shear.

#### Elasticity and Relaxation Time Measurements.

According to the Maxwell theory the deformation occurring when a visco-elastic material is strained can be broken down into two parts:

- (a) viscous flow which is non-recoverable, and
- (b) an elastic deformation which is recoverable.

It is, therefore, justifiable to speak of a modulus of rigidity of these materials. This has been measured on the Clark-Hodgman apparatus (see above) by a simple technique which, however, seems to give reproducible results good to about 10%. In practice, a torque of say 10<sup>9</sup> is applied by the torsion wire and the reading of the lower needle, indicating the deflection of the inner cylinder, is taken at once. That no measurable flow has taken place, i.e. part (a) is unimportant, is demonstrated by immediately releasing the torque, when the lower needle should return to zero. The modulus of elasticity can then be calculated from the instrument dimensions by the formula:

$$R = \frac{T}{2\pi r_1 L \theta} (1/r_1 - 1/r_2)$$

where L = length of inner cylinder

r<sub>1</sub> = radius of inner cylinder

r<sub>2</sub> = radius of outer cylinder

θ = angle through which inner cylinder is deflected

T = torque

R = modulus of rigidity

\*Possibly by hydrogen linking in the X-104 solutions:

Elasticity values for the common thickened fluids and some other materials are shown in Table II. They have been found to be independent of the radius of the inner cylinder used. For the Nopalms rise in temperature causes an increase in modulus of elasticity.

According to the Maxwell concept one other quantity is required to specify completely the properties of the material. This is the relaxation time, which can also be determined on the Clark-Hodgson instrument in the following manner. A twist of  $90^\circ$  is placed on the torsion wire and after the inner cylinder has swung through, say  $30^\circ$ , the torque may be decreased slowly by manually turning the upper torsion head so that the deflection of the inner cylinder remains constant at  $30^\circ$ . The time to reach torques of  $50^\circ$ ,  $40^\circ$ ,  $30^\circ$ ,  $20^\circ$  and  $10^\circ$  can be obtained with a stop-watch. A curve of deforming force  $F$  against time,  $t$ , can be plotted and from this by graphical differentiation a plot of  $F$  vs.  $dF/dt$  obtained. If  $T$  is a constant, this should give a straight line, from which  $T$  can be calculated by equation (6). In practice the relaxation times have been found to be variable. Figures 14 and 15, show the steps in the calculation and the variability of  $T$  with the imposed force. Approximate relaxation times for typical thickened fluids are also given in Table II.

#### Measurement of Elasticity at High Frequencies.

Early in the investigation it was thought that it might be, not the static rigidity and relaxation time which would be of importance, but their values at high frequencies. For this reason two methods for measuring these quantities at varying frequency were used.

a. The Ferry Method. This has been fully described in the literature\*. The method is optical in nature and depends upon the solution under investigation being optically clear and becoming birefringent under strain. Hence, it was only possible to make measurements upon the isobutyl methacrylate interpolymer gels. Results for these are shown in Table II, while Dr. Ferry made the following comments:

"1. Within experimental error there is no dispersion in any of these systems, so that the relaxation times involved are less than  $10^{-3}$  sec. in magnitude, and, in the case of 5A393, less than  $10^{-4}$  sec.

"2. The dependence upon concentration in the A3 series shows that at a given temperature the modulus of rigidity is approximately proportional to the third power of the concentration. A similar result was obtained for polystyrene, and attributed to increasing numbers of "points of entanglement" of the polymer chains with increasing concentration. This interpretation might apply to your systems and could facilitate explanation of the temperature

\* J. D. Ferry, J.A.C.S. 64, 1330, 1942



dependence, thus:

- "3. The dependence upon temperature shows that the rigidity increases rapidly with temperature, much more rapidly than the proportionality to absolute temperature which is theoretically characteristic of rigidity associated with orientation entropy. That the orientation entropy cannot contribute very much, anyway is shown by the concentration dependence.

My guess is that the number of "points of entanglement" is increasing with increasing temperature because the polymer is dissolved in a "poor" solvent -- in the sense discussed by Mark et al. in the last issue of the J.A.C.S. (64, 1557). The remarks in that paper on the temperature dependence of viscosity will also apply to a rigidity which is due to transfer of stress at points where polymer molecules come in contact."

The high frequency rigidities parallel the Clark-Hodgman rigidities, the 5A1-1 being weaker than the 3A3-2 for both tests. Furthermore, the rigidity is approximately proportional to the third power of the concentration in both instruments.

b. The Resonance Method. Dr. Sandvik and Mr. Goldberg of the Eastman Kodak Company Research Laboratory have developed a method for determining the rigidity and viscosity of viscoelastic materials at frequencies ranging from 5 to 70 cycles per second, corresponding respectively to effective rates of shear of 0.7 to 35 reciprocal seconds. This is done by measuring the response of a vibrating system, of which the liquid under test is a part, to sinusoidal forces of known amplitude and frequencies. The equations applying to such vibrations are simple and well known, and quantitative data may be derived comparatively easily from the shape of steady state resonance curves. This is an advantage over the method of Kendall\* where a torque of known magnitude is applied for a short time to the inner of two concentric cylinders containing the liquid and its motion recorded photographically. Such response curves are difficult to analyze mathematically since they deal with transient conditions.

The apparatus (Fig. 16) consists of an inner cylinder suspended by a silk fiber and centered at its lower end by a small hole and needle attached to the outer cylinder, which is surrounded by an outer thermostatic water jacket. The outer cylinder is accurately centered on the axis of rotation of a turntable, mounted on bearings and rigidly connected to a rocker arm. This is driven by a shunt motor through a cam and ball bearing. In this way the turntable can be given a truly sinusoidal motion at frequencies ranging from 5 to 70 cycles per second. The motion of the inner cylinder is followed by a mirror and light beam. The width of the light beam trace is measured as a

\* J. H. Kendall, Rheology Bulletin 12, 26, 1941

function of the frequency of the turntable determined stroboscopically. Several concentric cylinders were used so that the moment of inertia of the inner cylinder could be varied.

Consider the various resonant systems shown in Fig. 17. All contain two mass elements having moments of inertia, connected by a spring element with negligible mass, and a damping element causing loss of energy. A turning force or torque applied as indicated by T can cause distortion of the springs C accompanied by a viscous drag R. For such systems:

$$\begin{aligned} T &= M \, dv/dt \\ v &= dx/dt \\ dT &= dx/C \end{aligned}$$

and for truly viscous damping:

$$T = Rv$$

where T is the torque, M is the moment of inertia, v the angular velocity, x the angular displacement, C the compliance (angular deflection divided by torque), and R the damping of the liquid layer caused by viscosity. From these relationships the equations given in Fig. 17 can be derived. It may also be shown that the amplitudes of the displacements of the two masses,  $x_1$  and  $x_2$  are proportional to their velocities.

$$v_1/v_2 = x_1/x_2 = m$$

This amplitude ratio, m, is measured as a function of the frequency, f, giving curves similar to Figs. 18, 19, 20 and from these the compliance may be calculated:

$$C = 1/\mu_2 w^2$$

where  $w = 2\pi f$ . This holds only when damping is small, i.e.  $R_{max} > 3$ .

In order to derive the shear modulus of the liquid from its compliance, the liquid may be divided into three zones (Fig. 21). If:

- L = depth of immersion
- s = thickness of end layer
- $r_1, r_2$  = radii of cylinders
- F = shearing force
- S = surface of contact between adjoining layers
- G = shear modulus of the liquid
- C = compliance of liquid
- $dv/dx$  = shear

then:

$$dV/dx = F/sG$$

The compliance of part A of the liquid is (Fig. 21).

$$\begin{aligned} C_A &= \int dC_A = \int d\alpha / Fx \quad \text{where } d\alpha = dx/x \\ &= \int dx / Fx^2 \\ &= \int dx / Gsx^2 \\ C_A^A &= \int_{r_1}^{r_2} dx / 2\pi LGx^3 \end{aligned}$$

For part B one finds in a similar way:

$$C^B = \int_{r_1}^{r_2} \frac{(r_2 - r_1)}{2\pi LGx^3(x-r_1)} dx$$

For part C the engineer's torsion formula may be used:

$$C_C = 2s/\pi r_1^4$$

and the total compliance is given by:

$$C = C_A + C_B + C_C$$

When numerical calculations are made it is seen that providing the annular space between the inner and outer cylinders is not great ( $r_1-r_2$  about 0.9)  $C_B$  and  $C_C$  are small compared with  $C_A$  and

$$\begin{aligned} C &= C_A = 1/4\pi LG (1/r_1^2 - 1/r_2^2) \\ G &= \frac{1/r_1^2 - 1/r_2^2}{4\pi LG} \end{aligned}$$

Shear moduli of typical liquids calculated in this way are plotted in Fig. 22 against the effective rate of shear\* and are summarized in Table II.

\*The rate of shear which, if acting in a Newtonian liquid continuously, would cause the same dissipation of energy in the liquid as the varying rate of shear actually applied. For sinusoidal motion  $r_{eff} = \sqrt{2}/2 r$ . As the phase angle of the velocity ratio  $m$  of the two cylinders is equal to

90 at resonance, the modulus of that ratio at resonance is

$$/m/ = \sqrt{n^2 + 1}$$

or approximately  $/m/ \sim n$  for  $n > 8$ . Therefore the effective rate of shear acting in the vibrating system described in this report is

$$r_{eff} = n\dot{\gamma}/2(r_2 - r_1)^{1/2}$$

substituting numerical values:

$$r_{eff} = \omega n / 100 \text{ sec.}^{-1}$$

The finite height of the resonance curves shown in Fig. 18-20 is due to the dissipation of energy in the liquid because of its viscosity. In Fig. 17 it was shown that the numerical value of the viscosity necessary to account for the observed height of a resonance curve depends upon the position of the damping element in the vibrating system. An attempt has been made to find a mechanical model which would account for measurement made under steady shear and also for the shape of the curves obtained by the resonance method.

In Fig. 23(a) such a model is shown. The liquid is built up of units  $M_1$ - $M_2$  which can expand as stress is applied, and contract when it is removed. Their compliance  $C$  and damping  $R_D$  accounts for all the elastic properties of the liquid. However, if the shearing force be large, or applied steadily for long periods of time, separate units will slide over each other appreciably, causing permanent deformation. Assuming no breakage of the elastic units, steady shearing forces, as applied in an ordinary viscometer, cannot cause flow through  $M_2$  except for transient displacements shortly after the shearing force is changed (elastic fore- and after-effects). The viscosity measured in the classical instruments is, therefore, represented by  $R_S$ . The formula for  $R_D$  based on this model is shown in Fig. 23. By the use of  $R_S$  viscosity data, obtained in a steady-shear viscometer, numerical values of  $R_D$  can thus be calculated.

For the model shown in Fig. 23(a) both  $R_S$ , viscosity and shear modulus would be expected to vary in the same manner with concentration. This is brought out by Fig. 24. Both vary with about the third power of the concentrations \* and this function is independent of rate of shear.

Fig. 25 shows a log-log plot of  $R_D$  viscosities versus rate of shear. It will be noted that the slopes of the  $R_D$  viscosities are almost identical with those of  $R_S$  viscosities measured in the MacMichael viscometer although the values are much smaller. With the small amplitudes used in the present experiments no flow due to  $R_D$  would, therefore, be expected to occur. Some experiments were made with five-fold the amplitudes used here, but only slight difference in the resonance curves was observed. Nevertheless, at sufficiently high amplitudes a change in resonance characteristics must be expected.

\* It is interesting to note that, in the Clark-Hodgman experiments, the shear modulus was approximately proportional to the third power of the concentration.



### Thixotropy.

Many of the thickened materials have been found to exhibit thixotropy, this becoming particularly marked at low temperatures. It can readily be detected with Formula 241 on the McMichael and is easily demonstrated by the falling ball technique for X-104 thickened fluids.

When a steel ball is allowed to drop through a tube containing a Napalm or X-104 solution, an initial reading for the fall rate is obtained. If now the tube is immediately inverted and the travel of the ball again timed, the rate will be found to be much greater. However, if the tube be allowed to stand undisturbed for a period, the initial reading is regained and appears to be perfectly reproducible. The minimum standing time necessary or "recovery time" is indicated in Table III for several concentrations of Napalm. This phenomenon seems to be the same as the structure break-down and subsequent healing measured in the Jewell's latex viscosimeter.

TABLE III.

Recovery Times for 3, 6, and 12% Napalm

Concentration	<u>-10°F.</u>	<u>70°F.</u>	<u>150°F.</u>
3%	-	3-5 secs.	Immeasurable
6%	ca. 7 mins.	ca. 1.5 mins.	Very short
12%	30 mins.	4 mins.	Very short

At -10 F. the effect is so marked that the viscosities of these materials cannot be measured on the McMichael or Storer viscosimeters, the results being too confusing.

Precise measurement of this property, as indicated by change of viscosity on standing or stirring, is difficult so that in the ordinary viscosity determinations as far as possible equilibrium values of viscosity have been taken. Nevertheless, it must be remembered that many of the thickened fluids show this property to a greater or less degree.

### Shortness.

If one dips a hand into a mass of thickened fluid and withdraws it rapidly, the gel may string out showing considerable extensibility or may break off, in which case it is said to be short. This property variously known as "stringiness", "shortness", "extensibility", etc. appears to be important in the practical behavior of the thickened fluid. Short gels shatter and do not carry well either in the flame thrower or incendiary bomb at the same time they show lack of adhesion.



In an attempt to evaluate shortness, which admittedly has not been completely satisfactory, the following test was developed:

A glass tube of approximately 4 mm. internal diameter and having a ground glass joint at its midpoint is filled with the material under test. The lower end of the joint is held in a clamp (Fig. 26), the joint carefully loosened and the upper half raised at a constant speed of 0.5 inch per second. The distance between the two glass tubes at which breakage of the gel thread occurs has been defined as the extensibility. For a good "long" gel it will be greater than 2 inches, short gels may show values less than 0.5 inches.

A convenient method of making short gels of X-104 is to add small percentages of Polypale Resin (abietic acid dimer) to the solid X-104 before solution. Table IV shows values of shortness and Clark-Hodgman rigidity for a series with varying amounts of Polypale Resin. It appears to be generally true that short gels have higher rigidity though it is possible for gels with the same viscosity (as measured on the Stormer):

TABLE . I V .

<u>S a m p l e</u>	<u>Extensibility</u>	<u>Clark-Hodgman Rigidity</u>
8% X-104 in Versol	2.5 ins.	710 dynes/cm. <sup>2</sup>
8% X-104, 0.25% Polypale Resin in Versol	0.65 ins.	910
8% X-104, 0.5% Polypale Resin in Versol	0.5 ins.	890
8% X-104, 1% Polypale Resin in Versol	0.25 ins.	1290

to have differing extensibilities. X-104 gels as first made up tend to be short, their extensibility increasing rapidly over the first 24 hrs.

#### Work Hardening.

While attempting to evaluate the property or agglomeration of properties variously known as "stringiness", "shortness", "tensile strength", etc., it was found that certain of the gums exhibit work hardening, i. e., increased resistance to shear upon mechanical working. This can readily be seen by shaking a solution of an isobutyl methacrylate

interpolymer in either gasoline or Varsol\*, when the gum takes on a "jello-like" appearance and can be demonstrated to have a higher modulus of rigidity as measured by the Clark-Hodgman. When shaking is stopped, the change-back from "gel" to "sol" is fairly rapid, being almost complete in from one to two minutes. A semi-quantitative test was developed in which the height of drop required for a steel ball to penetrate a given depth of material was determined. After shaking, the height of drop required for penetration increased five or six-fold.

Work-hardening has been observed mainly on formulae of which the isobutyl methacrylate polymer AE or interpolymers are components. It does not appear to be found for mixtures of the type of Formula 241 or for the X-104's except when Polysole Resin is added. This again is in agreement with the picture that the isobutyl methacrylates give long fibrils which may be oriented by stirring to give strings or which can felt together upon shaking thus giving a "gel" or mass of increased rigidity.

#### Yield Value.

Precise determination of velocity gradients at low rates of shear in order to determine whether or not a material has a yield value is difficult. No thorough investigation of yield value has been made in this study but two qualitative tests appear to give an indication of whether or not a yield value is present in a particular material:

- a. The appearance of the surface of the material after long standing undisturbed in a container. If this be smooth, the material probably has no yield value.
- b. A blob of the material may be placed between glass plates, if it attains a definite radius and shows no further increase in this with time, then it has a yield value.

By these tests, materials of the type of Formula 241 appear to have a yield value. The other thickened fluids, except 10% pulped newspaper in 4% X-104 show none. This is in agreement with the fact that suspensions of solids in liquids usually show yield values.

\* A higher boiling petroleum fraction.

### Summary of Rheological Properties.

All the thickened fluids investigated have been found, without exception, to be non-Newtonian, with a rate of shear-shearing force curve convex to the shearing force axis. One group show little or no elastic after-recovery, the other may be classed as visco-elastic. Some may show a yield value. Nearly all have measurable moduli of rigidity as measured statically on the Clark-Hodgson apparatus or at varying frequency with the Ferry or resonance instruments. As measured by the two last methods the rigidity is independent of frequency or amplitude. Relaxation times as measured on the Clark-Hodgson vary from approximately 5 to 40 secs. and are not independent of deformation.

When subject to sudden shearing force, thickened fluids such as Formulae 122 and 241 reach their final viscosity almost instantaneously while the X-104 and isobutyl methacrylate interpolymers thickened fluids show a maximum deflection before coming to their equilibrium value. This maximum is dependent upon the time the liquid is allowed to stand before it is disturbed.

Thixotropy has been shown by some of the materials, both of the methacrylate and X-104 types. Dilatancy has not been observed although some of the methacrylate interpolymers thickened materials exhibit work-hardening.

Table V summarizes the properties of some of the liquids investigated, measurements being at 70°F. unless otherwise stated.

### Discussion.

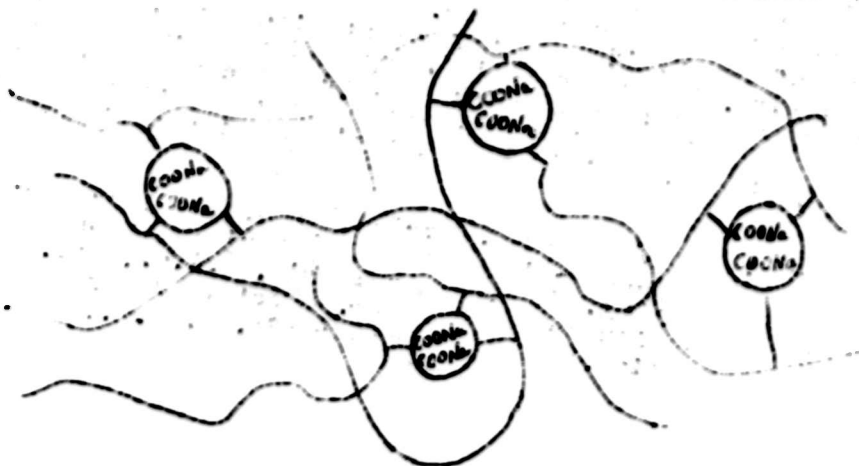
Precise study of the liquids of interest is rendered difficult by a number of factors. Samples from different sources or even from the same source give different results. X-104 gels are very sensitive to moisture in the solid X-104 and the drying conditions used in its preparation, a fact which was not appreciated until relatively late in the present work. All thickened fluids are apt to change in viscosity on keeping, this being particularly marked for the methacrylate interpolymers. Over and above these, development work on the thickening agents has been proceeding steadily during the period under review, making information, in some cases, obsolete almost as soon as obtained. These facts make the values quoted above only typical and may in some instances make the data not entirely consistent. However, the values obtained for correlation with the practical experiments described in Part II were obtained, wherever possible, on the same solutions and on the same day.

The behavior shown by the thickened fuels in the "jeweler's lathe" viscosimeter is of the greatest interest. Referring back to the sketch on p. 10, the MacMichael, pressure and other viscosimeters in which steady movement is attained presumably measure a viscosity comparable to  $D_0$ . The resonance viscometer, on the other hand, probably measures a viscosity more comparable to  $D_0$  since little or no flow occurs. We should, therefore, not expect agreement between the various methods employed.

The occurrence of a maximum appears to be connected with the presence of hydrocarbon chains in the liquid, as also manifested by elasticity. These chains may be pictured as a snarled, tangled mass, the individual chains being tied together at certain points of attachment by secondary valence forces. When subjected to sudden shear, these chains will tend to straighten and the points of attachment, as they come under strain, will break successively, accounting for the maximum in the deflection time curve. In some cases more stretch may be possible, e. g. the methacrylate interpolymers, giving a slow rise to the maximum, while in others, e. g., X-104 • Polynole Resin, there may be little uncurling of the chains possible, the points of attachment coming under strain and breaking almost immediately, thus giving a rapid rise to  $D_{max}$ .

The temperature coefficient is in agreement with the above picture, the activation energy found for X-104 being about that of the hydrogen linkage. For a basic aluminum soap the hydrogen link seems a very probable form of bond at the points of attachment.

For the interpolymer gels such a structure as that sketched seems very probable. The polar carboxyl groups of the copolymerized methacrylic acid would tend to lie in the water globules, giving a ball and chain structure to



the gel. Under shear, the chains would tend to straighten and the carboxyl groups, functioning as points of attachment, would be pulled from the water spherules. This is in agreement with the much greater times required by the interpolymer gels to reach  $D_{max}$ . Recovery of the above structure might be expected to be much slower than recovery of a structure formed by molecular forces as in the X-104 gums. This is found to be true experimentally. Also prima facie evidence for the above are the facts that the interpolymer dissolved in gasoline alone gives a Newtonian liquid, alcoholic caustic potash will not give a gel although one can be made to form if sufficient water be added subsequently.

With Formula 241 and similar gels it seems possible that the high viscosity may be due largely to mechanical interference of the water spherules suspended in a highly viscous medium. No peak or  $D_{max}$  would be expected from such a system on the "jeweler's loche" viscosimeter.

In the resonance or oscillation viscosimeter since the displacements are very small and short in duration no breakage of points of attachment between the chains would be expected, movement of segments of the tangled mass through the liquid menstruum with possibly some uncurling of the chains alone would occur. A higher modulus of rigidity and lower viscosity than in static experiments would be expected. Such behavior is found to be expressed by a spring and dash-pot model. This was found to be true except that the rigidity modulus and viscosity obtained by both the resonance and Ferry methods are practically independent of frequency. Such a result would not be expected from equations based on statistical mechanics\* but has also been observed experimentally with other polymers.\*\*

To summarize, the thickened fluids found to be of interest thus far are pseudoplastic and show no peculiar changes in rheological behavior when measured at frequencies of from 5 to 500 cycles/sec. The elastic properties of some of the fluids are consistent with a tangled chain structure, the chains being anchored to each other at points of attachment by secondary valence forces or in some cases possibly being anchored to water spherules by the polar carboxyl groups of the copolymerized methacrylic acid.

\* A. Tobolsky and H. Eyring "Rheological Properties of Rubber-like Materials" Society of Rheology Meeting, Hotel Pennsylvania, N.Y.C., Oct. 30, 1942.

\*\* Discussion on above paper. Society of Rheology Meeting. Hotel Pennsylvania, N. Y.C., Oct. 30, 1942.



P A R T I I.

UNIGNITED JET AND BOMB EXPERIMENTS.

1/8" Jet Experiments.

A small model cylinder and 1/8" nozzle have been built to obtain unignited ranges\* for pressures up to 1000 pounds/square inch. This was similar to that previously described by Hottel and Garraway\*\* except that an indicator arm was attached to the piston, allowing the rate of travel of the latter to be determined. Figure 27 shows the whole apparatus ready to run, while Figure 28 shows cylinder and indicating mechanism in more detail. The nozzle is inclined at an angle of 7° to the horizontal and is so mounted that it can be rotated according to wind direction. The cylinder A is charged from the reservoir B, containing the liquid under investigation, by means of pressure. The nitrogen pressure in cylinder C is adjusted to the desired value and the charge fired by opening the valve D. The travel of the piston is recorded by the silver solder stylus E recording on a sheet of baryta-coated paper on the rotating drum, F, driven by synchronous motor; G. Nozzle velocity was also measured in some cases by high speed photography (1500 frames per second) of the jet. Good agreement between the two methods was obtained. Range was measured wherever possible by actual observation of the point where the stream struck the ground. With liquids of low viscosity, however, atomization is so great that the range must be estimated while the jet is in the air. All range determinations were made by the same observer so that they are believed to be consistent and good to  $\pm 4$  ft.\*\*\*

Range data for the liquids investigated are given in Appendix II together with jet velocities at the nozzle.

The appearance of the liquid stream as it leaves the orifice is of considerable interest. Newtonian liquids of low viscosity, e.g. gasoline, even at a pressure of 100 lbs./sq. in. are completely broken up at the orifice and form a fine spray (Fig. 27b). Newtonian liquids of intermediate viscosity, 1 to 10 poises, while completely atomized at the higher pressures, say 600 to 1000 lbs./sq.in., issue

\* While it is fully realized that ignited jets have considerably greater ranges than unignited, due to the lowered density of the warm air, the factors influencing break-up of the jet must remain the same. Therefore, any conclusions drawn as to the most desirable physical characteristics for a thickened fluid for maximum range, will probably remain valid for ignited fuels.

\*\* Joint Report on "Status of NDRC Projects on Flame Throwers." 6/24/42.

\*\*\* Wind greatly affects range. The runs always were made with the wind, the velocity of which was not greater than 1-3 m. p. h.

as a smooth stream at lower pressures, finally breaking up 2 to 6 ft. away from the nozzle (Fig. 28b). Newtonian liquids of high viscosity show no break in the stream or atomization at pressures up to 1000 lbs./sq. in.

X-104 thickened fluids behave like the Newtonian fluids of intermediate viscosity. That is, at higher pressures, there may be some break-up of the jet. This is not found for the most concentrated solutions.

The isobutyl methacrylate thickened gums show no atomization. The 5% isobutyl methacrylate (0.1% interpolymer) comes out as a continuous stream at low pressures (100 to 400 lbs./sq.in.), separating into "snakes" at 2 to 4 ft. from the nozzle. These then pull together into spheres. At higher pressures (1000lbs./sq.in.) a break in the stream occurs similar to that shown by Newtonian liquids of intermediate viscosity.

#### Factors Influencing Range.

The important factors influencing range would seem to be (1) the initial kinetic energy of the jet which dictates the maximum possible range, (2) the frictional drag of the air which ultimately causes jet break-up and prevents attainment of the maximum possible range.

Both of these will be dependent upon the physical properties of the extruded liquid. It is desired to know which of them, among those described in Part I of the present report, are of significance.

#### The Initial Momentum of the Jet.

For a given nozzle, the initial velocity of the jet,  $V$ , will be dependent upon the applied pressure,  $P$ , the viscosity,  $\eta$ , and density,  $\rho$ , of the liquid. Thus,

$$V = C \sqrt{2gP}$$

where  $P$  is expressed in feet of fluid flowing and  $C$  is the discharge coefficient. When the discharge coefficient is plotted against the Reynold's Number  $DV\rho/\eta$ , where  $D$  is the diameter of the nozzle, a smooth curve is obtained indicating that  $C$  and hence  $V$  is a function of the density and viscosity of the liquid under test. Such was found to be the case in the present investigation when the data for the Newtonian liquids were plotted.

For non-Newtonian liquids it might be expected that the discharge coefficient and hence the nozzle velocity and initial kinetic energy would be governed by the apparent viscosity of the liquid at the rate of shear met in the

orifice. This is undoubtedly high and probably corresponds to rates of shear commensurate with those found in the high pressure capillary viscosimeter (p. 6). The initial velocities found do, in fact, correlate at least qualitatively with the apparent viscosities measured at a rate of shear of 4000 reciprocal seconds, (Fig. 29). The only serious discrepancy appears to be for the dilatant starch-glucose-glycerol mixture, which has much higher initial velocities than would be predicted from its viscosity-rate of shear relationship. This may be due to plug flow at high pressures, a layer of liquid lubricating the passage of a plug through the orifice.

To attain the same initial kinetic energy,  $\rho V^2/2g$  ft. lbs./cu.ft., from a liquid of high viscosity it will be necessary to use a greater pressure than for a liquid of low viscosity. Hence, it is important to compare ranges at equal initial kinetic energies rather than equal pressures, particularly because the discharge coefficients of the pseudoplastic materials cannot be predicted. Therefore, in the following where ranges are to be compared,  $V^2$  will be used rather than pressure.

#### Jet Break-up.

On pp. 4 and 5 a number of physical properties which might control jet break-up due to the shearing action of the air were listed. Any practical flame thrower is probably restricted to the use of hydrocarbon or coal tar fuel, for such materials large variations in density or surface tension are probably impractical but viscosity may be varied over at least a thousand-fold range by the incorporation of solid fillers or by the solution of thickening agents. Hence, the liquids used in the present study were picked in such a way as to cover a wide viscosity range and to allow simultaneously the importance of the variables 4-9 of p. 5 to be ascertained.

The phenomena described above undoubtedly indicate that viscosity plays a considerable part in controlling range even before the liquid meets the air. Calculation shows that liquids such as gasoline which are completely atomized at the nozzle are in turbulent flow through the orifice; while, at comparable pressures, liquids of higher viscosity which undoubtedly flow through the orifice in viscous motion give a smooth stream. It seems reasonable to believe that if the jet issues from the orifice in turbulent flow, its air resistance will be greatly increased and its range shortened. If, on the other hand, it issues as a smooth stream even although its initial momentum may be lower its range may be greater. With liquids of low viscosity, therefore, there is probably an optimum pressure for range. This should move toward higher and higher pressures with rising viscosity. For liquids of medium viscosity no maximum range may be observable.



In Fig. 30 range is plotted versus  $\rho V^2$  (proportional to the initial kinetic energy) for the Newtonian liquids of low viscosity. As predicted in the last paragraph, some of the curves pass through a maximum which seems to occur at higher momentums with increasing viscosity. With these types of jet it seems likely that surface tension also plays a considerable role since the glycerol solutions show high ranges for their viscosity. In the curves of Fig. 31, the range passes through no maximum but increases steadily with viscosity until blown castor oil is reached. These liquids also show no break-up at the nozzle.

On Fig. 32 results for the X-104 thickened fluids are plotted. This graph should be studied in conjunction with Fig. 5 on which the apparent viscosities of the materials under test are plotted against rate of shear. 2% X-104, while it does not break up at the nozzle, shows ranges comparable to boiled linseed oil, which has approximately the same viscosity. It will be noticed on Fig. 5 that the viscosity curves of polyvinyl alcohol and Karaya Gum cross at approximately 50 reciprocal seconds. On Fig. 32 their range curves cross. On Fig. 5 the viscosity curves of blown castor oil and 6% X-104 cross at approximately 16 reciprocal seconds, while on Fig. 32 the range curves again intersect. All the range curves lie in order of their viscosities or apparent viscosities, hence it seems plausible to reason that the principal property of the liquids affecting the air drag is viscosity. If we assume that at the point of intersection of the 6% X-104 and blown castor oil range curves the rate of shear is 16 reciprocal seconds and the viscosity of the two liquid streams 190 poises, then the shearing force exerted by the air is 3040 dynes/cm.<sup>2</sup>. This is of a reasonable order of magnitude since, if we assume that the stream travels as a cylinder from the jet to the ground which it reaches with zero velocity, the shearing force required would be of the order of 1500 dynes/cm.<sup>2</sup>. These are both rough calculations and probably no better agreement could be expected.

The isobutyl methacrylate interpolymers thickened fluids, results for which at equal initial kinetic energy are plotted in Fig. 33, once again fall in order of their viscosities. The Karaya Gum and 2% isobutyl methacrylate\* fall in the right position if we assume that the curves obtained on the Clark-Hodgson intersect at higher rates of shear. Unfortunately, no reliable data could be obtained for the isobutyl methacrylates on the MacMichael viscosimeter owing to their high elasticity and tendency to wind themselves around the inner cylinder suspension. At comparable momentums the

\* The peculiar shape of the 2A3-2 curve is probably due to wind, which sprang up while the attempt was being made to finish the series.

sample of Formule 241 weighted with powdered lead showed a greater range than the unleaded gum but this may be explained by the higher viscosity of the former.

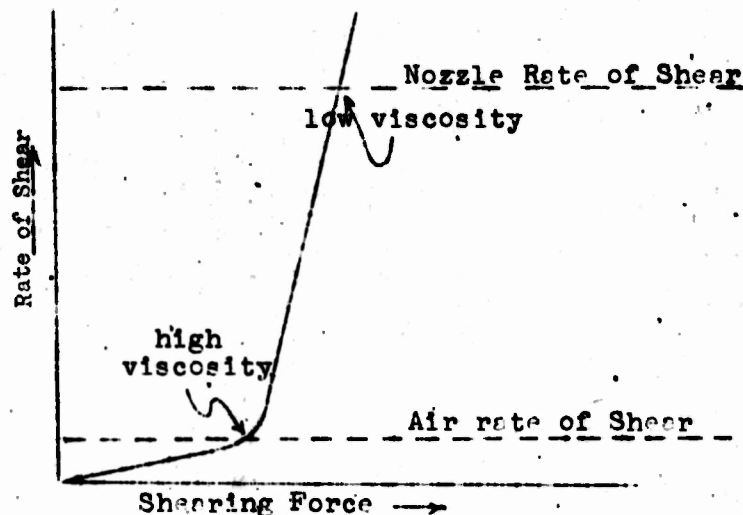
From the data of Figures 30-33 and 5 it would appear that the velocity gradient effective on the liquid stream while it is passing through the air varies from 15 reciprocal seconds at low to 50 reciprocal seconds at high initial kinetic energies. For a  $V^2/\rho$  value of 50,000, the maximum attained by the most viscous, Newtonian liquid, the corresponding rate of shear would be about 30 reciprocal seconds. Fig. 34 shows a plot on semi-log paper of range at an initial kinetic energy equivalent to  $V^2/\rho = 50,000$  vs. apparent viscosity (poises) measured on the MacMichael viscosimeter at this rate of shear. With the exception of water, the glycerol solutions and liquids of very low viscosity which are atomized highly, a good straight line is obtained. Also shown on the plot is a point for leaded 241. This might be expected to be higher than the curve, since at the same momentum, the velocity will be considerably lower with consequent reduction in air resistance. Considering the wide range in viscosities, the different nature of the materials studied and the uncertainties in range determination, the correlation is remarkably good.

Plotted on Fig. 34 are liquids of all types, the wide variation in their properties being summarized in Table V. Included are Newtonian liquids with viscosities varying from 0.006 poises to 190 poises, pseudoplastic liquids with pronounced rigidity, a dilatant mixture\*, and pseudoplastic material having a yield value. Qualitatively, the results for the isobutyl methacrylate thickened gels which show work hardening are also in agreement. This does not mean that other factors may not at times become important. Thus, X-104 thickened fluids with high "shortness", i.e. low extensibility, p. 17; give lower ranges than "long" gels probably because they resemble too closely in properties a true solid. Thus, they show a relatively high modulus of rigidity and the stream in the air appears to shatter or crumble into fragments rather than adhere together. Nevertheless, except for liquids of high surface tension or very low viscosities, the conclusion seems inescapable that at equal initial kinetic energies, range is mainly a function of apparent viscosity measured at the rate of shear appropriate to aerial drag.

We can now explain why thickened fuels are so satisfactory for use in the flame thrower. An ordinary Newtonian fluid of high viscosity may give very satisfactory range at high enough momentum; this, however, cannot be attained

\* Stormer viscosities for this mixture were obtained because it was immeasurable on the MacMichael viscosimeter. The absolute rate of shear on the Stormer was determined by calibration with a non-Newtonian liquid which had previously been measured on the MacMichael.

except by the use of excessively high pressures. Thus, with a polyglycerol solution, having a viscosity of 9000 poises which would be ideal to prevent break-up of the jet by the air, the  $V^2/\rho$  attainable at 1000 lbs./sq.in. pressure was only 43. Pseudoplastic materials, on the other hand, give a low apparent viscosity at high rates of shear, allowing high initial kinetic energies to be attained. At low rates of shear high apparent viscosities are shown, which apparently are effective in preventing break-up of the jet.\*



Practically, therefore, the following tentative conclusions may be reached. Determinations of the apparent viscosity of a liquid under test for use in a flame thrower should be made over two ranges of rate of shear, namely from 5 to 1000 reciprocal seconds and 1000 to 10,000 reciprocal seconds. In the first range the apparent viscosity should not be less than 500 poises, in the second it should not be greater than 20 poises. Such tests do not, of course, allow any prediction of ignitability, ignited range, etc., but may still be useful in the development of new materials.

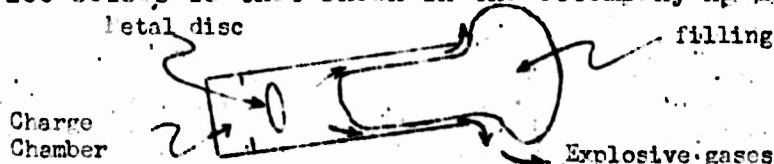
\* The dilatant mixture of starch-glucose-glycerine also gave a good range. Even at low rates of shear its viscosity is very high, of the order of 8000 poises. At the high rates of shear encountered in the orifice the apparent viscosity would be expected to be so great that the initial kinetic energy would be very small (less than that for polyglycerol). The relatively high initial kinetic energies obtained indicate that there must have been slippage, the material being forced through the orifice as a plug. Whether all dilatant materials would behave in this manner allowing practical initial kinetic energies to be obtained is an open question.

### M-56 Incendiary Bomb Experiments.

It has not proved possible to make as many experiments with bombs as with the flame thrower and those made have been restricted entirely to the M-56 incendiary bomb fired statically at a target or in the open field. For the former the bomb is set up 30 ft. away from and pointing at a vertical ply-wood target. After firing, the proportions adhering to the target and at its base are estimated. In the open field test, a bomb is placed on the ground at an angle of  $30^\circ$  to the horizontal and fired. The amount of scatter and distance traveled by the bomb contents are noted. For these test methods and the following firing test results we are indebted to the N.D.R.C. group at the Standard Oil Development Company, Bayway, New Jersey.

A number of materials of known rheological characteristics have been placed in casings and fired. Results are shown in Table VI.

Presumably the mechanism of ejection from the M-56 for liquids whose effective viscosity is less than about 100 poises is that shown in the accompanying diagram:



The disc sealing the explosive charge chamber cut its way through the Newtonian liquids of viscosity greater than 100 poises leaving an annular ring of fluid adhering to the casing wall. Apparently the explosion gases are incapable of forcing the liquid out if its viscosity is too high and must seek their release behind the metal disc. Pseudo-plastic materials, on the other hand, invariably leave the casing entirely clean indicating that the rate of shear must be such that their apparent viscosity is reduced to 100 poises or less. With filling materials of very low viscosities the gases may be able to make their escape through the liquid too readily, atomizing some of it and failing to give the remainder adequate momentum. This causes a large proportion of the filling to be deposited in front of the casing, e.g. blown castor oil.

Once out of the casing, the material is subjected to shear by the air and the case becomes analogous to the flame thrower. There are, however, two differences, first, the blob of material is much larger, and, second, its speed is only about one-fifth of that of a flame thrower jet.

Thus; the shearing force due to the air should be smaller and it would be expected that lower viscosities than those required in the flame thrower would be sufficient to insure arrival in an unbroken mass at the target. This does not seem to be entirely true. Among the Newtonian liquids, polyglycerol of about 500 poises was the first to carry adequately to the target with little break-up of the gob. The satisfactory fillings in practice, 8% X-104, 4% X-104 + 10% newspaper pulp and Formula 241, all have apparent viscosities of the order of 500 poises at 30 reciprocal seconds, and at lower shears their viscosities must be somewhat greater. In field tests, as in target tests, they behave similarly. This discrepancy may be due to the compression of the charge by the explosive wave, followed by its tendency to expand and shatter after release from the casing. This may result in a higher apparent viscosity being required than would be expected to be adequate to resist serial shear.

However, the results, limited as they are, suggest that the requirements for a good M-56 incendiary filling may be tentatively described as the possession of a pronounced pseudoplastic curve with an apparent viscosity at the casing rate of shear about 150 poises and at the air rate of shear about 700 poises. In order to evaluate this theory and, if correct, to fix these limits, considerable further work is required. Consultation of Tables V and VI shows that although the rheological properties, i.e., thixotropy, behavior on the jeweler's lathe viscosimeter, etc. of satisfactory thickened fluids are extremely varied, the apparent viscosity, as outlined above, is not the only factor. "Short" X-104 gels, e.g. (10) in Table VI, are unsatisfactory breaking up in flight and scattering. As in the case of the flame thrower, this may be because their properties resemble too greatly those of a solid, the explosion wave causing them to shatter.

Once the filling has reached the target, the factors influencing adhesion are not so clear. It appears certain that the following requirements must be met:

1. It must be soft enough so that the impact of the mass upon the wall will flatten it out into a firm, thin layer without too much fracture.
2. It must have a yield value or at least a high enough apparent viscosity at low rates of shear so that the mass after being flattened out on the wall will not run off too rapidly.
3. It must have a little stringiness. This should be low enough so that it will not bounce off the wall and preferably low enough so that the flattened mass will not



draw together again after being flattened and fall off. The exact rheological properties required to produce the above qualities have not yet been entirely determined. Formula 241 and 4% X-104 + 10% newspaper pulp both show a yield value which may prevent drainage from the target. There appeared to be satisfactory wetting in all cases where sufficient time in contact with the target occurred, but some fillings with high rigidity, e.g. the 7% X-104 + 1% Polysale Resin, bounce off the target immediately upon impacts.\*

At the present time, therefore, it seems that the chief requirement for an incendiary bomb filling is identical with that for a flame thrower liquid, pseudoplasticity. Other factors, imperfectly understood, are, however, undoubtedly important. Chief of these are those influencing adhesion.

\* Considerable light upon the behavior of bomb fillings is given by the empirical "dropping test." High speed movies have indicated that the velocity of the charge through the air after leaving the casing is of the order of 50 ft. per second. The impact on the target, therefore, may be duplicated by dropping the material from a height such that it reaches a target on the ground with a terminal velocity of approximately 50 ft./sec. Tests are made dropping 50 grams of the material so that they hit a piece of plywood inclined at an angle of  $45^\circ$  to the vertical. Short gums bounce and fail to adhere and, in general, the results of this test very closely parallel actual firing tests.

T A B L E    I I

RIGIDITIES AND RELAXATION TIMES OF SOME THICKENED FLUIDS AT 70°F.

		Clark- Hodsman	Resonance 5-40 Cycles/sec.	Ferry 160-500 Cycles/sec.	Relaxation Time
4% X-104	25 dynes/cm. <sup>2</sup>	-	-	-	-
6% X-104	300	550	-	17-21 sec.	
8% X-104	700	1450	-	-	
9% X-104	1400	2200	-	10-16 sec.	
12% X-104	3390	4250	-	6-18 sec.	
13.5% X-104	5300	-	-	30 sec.	
13.5% Napalm	2530	-	-	6-18 sec.	
4% X-104 + 10% Pulped None Newspaper		21,000	-	-	
Formula 122	None	-	-	-	
Formula 241	2600	30,000	-	-	
2% Isobutyl Methacry- late 0.3% I. P.	24	-	97 (87°F.)	5-10 sec.	
3% "	210	-	670 (84°F.)	-	
5% "	1020	1250	1480 (61°F.)	40 sec.	
3% Isobutyl Methacry- late 0.1% I. P.	3	-	-	-	
5% "	185	700	306 (77°F.)	16-30 sec.	

TABLE V

Material	Rheological Type	Viscosity at 30 sec. (MacMichael)		Viscosity at .015 sec. (Clark-Hodgman)		Rigidity (Clark-Hodgman) dynes/cm. <sup>2</sup>	Rigidity 5-40 cycles/sec. (Resonance)		Rigidity 160-500 cycles/sec. (Ferry)	Relaxation Time (Clark-Hodgman)	Max. -1 at 140 sec. (Jeweler's Lathe)	Thixotropy.	Yield Value	Work-Hardening
		poises	poises	poises	cm. <sup>2</sup> dynes		cm. <sup>2</sup> dynes	cm. <sup>2</sup> dynes						
Gasoline	Newtonian	.008												
Water	"	0.01												
Aqueous Glycerol	"	0.6+												
Aqueous Glycerol	"	3.6+												
Blown Linseed Oil	"	0.6+												
40 S.A.E. Oil	"	4.1+												
70 S.A.E. Oil	"	5.6+												
Castor Oil	"	5.45+												
Castor Oil + blown	"													
castor oil	"	52.5												
Castor Oil + blown	"													
castor oil	"	98												
Blown castor oil	"	190+												
40% Butyl Methacrylate in Gasoline	"	130												
Polyglycerol	"	9000+												
8% Pentonite in Thixotropic water	"					Very small						Yes	?	No
Pseudoplastic														
Starch-glucose-tila-		30,000		3.5+		0						No	None	No
Glycerine														
2% Faraya Gum in water	Pseudoplastic	13.3		1850		530								
Polyvinyl Alc.														
in water	"	52		85		0								
13.5% Napalm	"			12,200		2530				6-18	Present	Yes	None	No
4% X-104	"	13.5		24		25				-		Yes	None	No
6% X-104	"	140		2700		300				17-21	32	Yes	None	No
8% X-104	"	610		-		700				-	124	Yes	None	No

TABLE V (Con't)

7% X-104 + 1% Polypale Resin	-	-	1300	950	-	864	Yes	None	Yes
9% X-104	620	21,800	1400	2200	10-16*	264	Yes	None	No
12% X-104	1950	41,000	3390	4250	5-18	1100	Yes	None	No
13.5% X-104	-	55,500	5300	-	30	-	?	Yes	No
4% X-104 + 10% Pseudoplastic 280	-	-	No clarity	-	-	-	-	-	-
Pulped Newspaper	-	-	"	-	-	None	No	Yes	No
Formula 122	365(?)	-	-	-	-	-	-	-	-
15% isoButyl Methacrylate	-	37,200	1730	-	8-30	-	-	-	-
FR in Gasoline	-	-	-	-	-	-	-	-	-
Formula 241	490	18,900	2600	-	-	None	Yes	Yes	No
Leaded Formula 241	850	-	6800	30,000	-	None	Yes	Yes	No
A-2598	-	15,000	1800	-	-	Very small	Yes	Yes	No
A-2600	-	8,200	630	-	-	None	Yes	Yes	No
2% IsoButyl Methacrylate	-	600	24	-	97(87°F) 5-10	Present	?	No	Yes
late 0.3% Interpolymer	-	-	-	-	-	-	-	-	-
3% IsoButyl Methacrylate	-	8,000	210	-	670(84°F) -	Present	?	No	Yes
late 0.3% Interpolymer	-	-	-	-	-	-	-	-	-
5% IsoButyl Methacrylate	-	11,500	1020	1250	1480(61 F) 18-40	Present	?	No	Yes
late 0.3% Interpolymer	-	-	-	-	-	-	-	-	-
3% IsoButyl Methacrylate	-	-	3	-	-	Present	?	No	Yes
late 0.1% Interpolymer	-	-	-	-	-	-	-	-	-
5% IsoButyl Methacrylate	-	4,150**	185**	700	306(77°F)** 16-30	Present	?	No	Yes
late 0.1% Interpolymer	-	-	-	-	-	-	-	-	-

\* Measured at 80°F

\* Measured on Napalm not X-104

\*\* Values for a different sample from that shown in Fig. 5

\*\* Extrapolated

TABLE VI

<u>M a t e r i a l</u>	<u>Character</u>	<u>Apparent Viscosity 70 F., 30 sec.<sup>-1</sup></u>	<u>R e s u l t s .</u>
1. Blown Castor Oil	Newtonian	96 poises	Casing cleared, much oil atomized, some liquid left in front of casing.
2. " "	"	250	As (1) but some oil reached target.
3. Polyglycerol	"	450	Considerable polyglycerol left in casing, metal disc probably cut through charge. Little atomization, some liquid in front of casing. Considerable scatter in droplets 2 cm. radius.
4. " "	"	910	20% liquid on target. Metal disc cut through charge leaving considerable liquid in casing. Less scatter than in (3) No atomization.
5. " "	"	4200	Metal disc cut through charge, leaving annulus of polyglycerol in casing. 30% traveled through air as a mass.
6. " "	"	9000	Metal disc cut through charge leaving annulus of polyglycerol in casing. None atomized, all material leaving casing on target.
7. Bentonite	Thixotropic About Pseudoplastic 10		Casing cleared. Considerable atomization. About 20% of filling reached the target and stuck to it.
8. Starch-glucose-Dilatant		8000	Casing spun in the air so that 40% on target, 30% on wall behind original casing position. Material on target at first solid, started to flow after 30 secs. Little left in casing.



<u>M a t e r i a l</u>	<u>Character</u>	<u>Apparent Viscosity 70 F., 30 sec. -1</u>	<u>R e s u l t s .</u>
9. 8% X-104	Pseudoplastic	500 poises	Fair Adherence. No scatter. About 40% on target, 40% at base.
10. 7% X-104 + 1% Polypale Resin "short"	"		Considerable scatter. About 10% on target. Poor adhesion with bounce from the target.
11. 4% X-104 + 10% Newspaper Pulp.	Pseudoplastic Yield Value	520	About 20% scatter. 70% on target. Excellent adhesion.
12. F-241	Pseudoplastic Yield value Thixotropic	490	Some scatter. 55% on target. Good adhesion.

\* The filling is charged into the casing in a thin cheesecloth bag, the mouth of which is tied with string.

## APPENDIX I.

### N a p a l m.

Basic aluminium soap of naphthenic and palmitic acids. Prepared by milling the solid soaps at 95°C. followed by solution in gasoline at room temperature. This has been superseded by

### X-104.

Basic aluminium soap of naphthenic, oleic, and coconut oil fatty acids prepared by precipitation of an aluminium salt with the sodium salts of the acids in aqueous solution. Drying conditions and moisture content greatly influence the properties of the gum resulting when the dried salt is dissolved in gasoline.

### Isobutyl Methacrylate NR.

This is a normal isobutyl methacrylate polymer used in Formula 241.

### Isobutyl Methacrylate AE.

This is prepared by oxidation of the NR polymer so that some carboxyl groups result.

### Isobutyl Methacrylate Interpolymer.

These are prepared by copolymerization of the methacrylate with 0.1 to 0.3% methacrylic acid. In making up solutions, they are dissolved in gasoline, stirred for 15 mins. and 1% of caustic soda in the form of a 40% aqueous solution added. In the code used in the present report the first digit indicates the percentage polymer used, A indicates isobutyl methacrylate, the second digit the percentage of copolymerized methacrylic acid and the remaining digits the identification of the particular solution. Thus 3A3-2 indicates 3% isobutyl methacrylate 0.3% interpolymer the second solution prepared.

### Formula 241, A-2598, etc.

Code No.	Gasoline	% Poly- mer.	Polymer Kind	Stearic Acid	Naph- thenic Acid.	Wood Rosin	40% Aqueous Caustic Soda	Caster Oil.
F-241	87.0	5	NR	2.5	2.5		3	
F-122	88.0*	-	-	3.5	-	1.75	3	3.0
A-2598	87	5	AE	2.5	2.5	-	3	
A-2599	89	3	AE	2.5	2.5	-	3	
A-2600	90	2	AE	2.5	2.5	-	3	
A-2601	88.75	3	AE	3.5	-	1.75	3	

\*150° flash kerosene

# A P P E N D I X   I I

<u>M a t e r i a l</u>	<u>lb./in.<sup>2</sup></u>	<u>Nozzle Velocity Ft./Sec.</u>	<u>Range</u>
Gasoline - - - - -	200	185	35'
	400	225	"
	600	286	"
	800	319	"
	1000	323	"
W a t e r - - - - -	100	130	28'
	200	170	28'
	400	222	30'
Raw Castor Oil - - - - -	200	147	40'
	400	203	57'
	600	241	52'
	800	287	52'
	1000	317	53'
40 S. A. E. - - - - -	100	126	38'
	200	166	43'
	400	215	44'
	600	256	52'
	800	289	54'
	1000	317	65'
Boiled Linseed Oil - - - - -	100	139	40'
	200	166	47'
	400	230	37'
	600	260	40'
	800	340	46'
	1000	323	46'
Starch-Glucose-Glycerine - - - - -	200	70	56'
	400	130	86'
	600	165	110'
	1000	235	110'
Polyvinyl Alcohol in Water - - - - -	200	111	50'
	400	148	62'
	600	185	70'
	800	225	70'
	1000	273	75'
2% Karaya Gum - - - - -	200	175	67'
	400	231	72'
	600	287	76'
	800	320	80'
	1000	362	86'

<u>Material</u>	<u>"/in.<sup>2</sup></u>	<u>Nozzle Velocity Ft./Sec.</u>	<u>Range -</u>
Blown Castor Oil - - - -	200	67	32'
	400	123	60'
	600	174	75'
	800	222	80'
	1000	239	85'
70 S. A. E.	100	131	47'
	200	167	49'
	400	220	61'
	600	254	67'
	800	287	68'
	1000	317	71'
Bentonite 10% - - - - -	1000	315	56'
Formula 241 - - - -	100	82	33'
	200	107	46'
	400	174	73'
	600	222	81'
	800	270	93'
	1000	298	90'
Loaded 241 - - - -	400	148	80'
	600	171	105'
	800	189	115'
	1000	208	131'
4% X-104 + 10% Pulped News- paper	600	271	99'
Aqueous Glycerol - - -	200	160	57'
	400	189	57'
	600	230	82'
	800	250	73'
	1000	277	73'
Aqueous Glycerol - - -	200	167	64'
	400	194	64'
	600	232	71'
	800	264	68'
	1000	292	78'
Polyglycerol - - - -	1000	6	0.5'
2% Isobutyl Methacrylate - -	100	133	75'
0.3% I. P.	200	176	75'
	400	238	70'
	600	285	80'
	800	340	90'
	1000	333	90'

<u>Material</u>	<u>#/in.<sup>2</sup></u>	<u>Nozzle Velocity Ft./Sec.</u>	<u>Range</u>
3% Isobutyl Methacrylate 0.3% I. P.	100	112	60'
	200	147	80'
	400	209	85'
	600	254	96'
	800	297	90'
	1000	327	90'
5% Isobutyl Methacrylate 0.3% I. P.	100	100	45'
	200	121	56'
	400	179	87'
	600	230	98'
	800	266	105'
	1000	303	102'
5% Isobutyl Methacrylate 0.1% I. P.	100	77	27'
	200	99	50'
	400	136	80'
	600	173	103'
	800	219	103'
	1000	252	105'
2% X-104 - - - -	100	151	37'
	200	191	32'
	400	256	45'
	600	287	45'
	800	320	46'
	1000	347	46'
6% X-104 - - - -	100	128	63'
	200	166	68'
	400	238	75'
	600	273	80'
	800	311	85'
	1000	354	85'
9% X-104 - - - -	100	115	64'
	200	163	76'
	400	227	85'
	600	273	91'
	800	314	102'
	1000	344	101'
12% X-104 - - - -	100	97	73'
	200	144	80'
	400	216	89'
	600	254	98'
	800	292	101'
	1000	317	116'



Figure 1

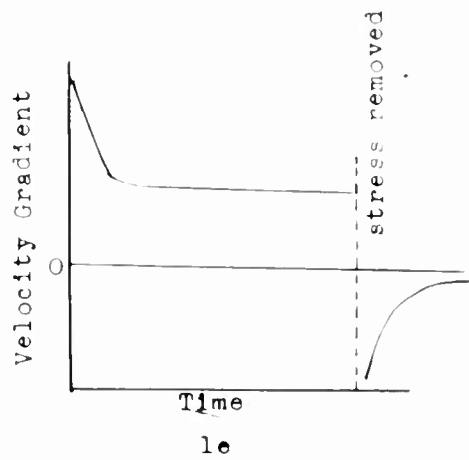
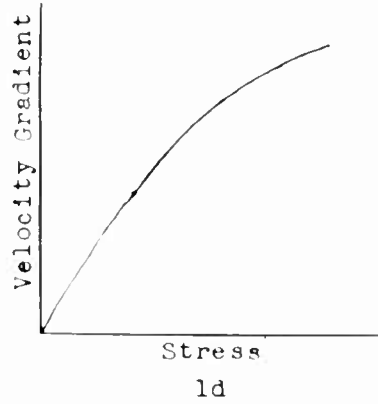
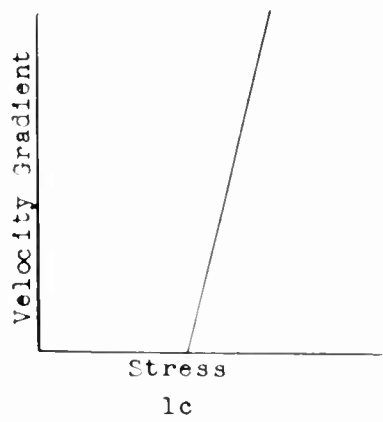
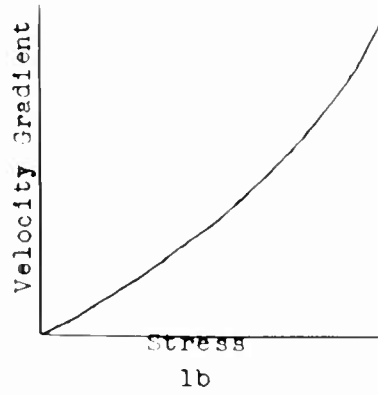
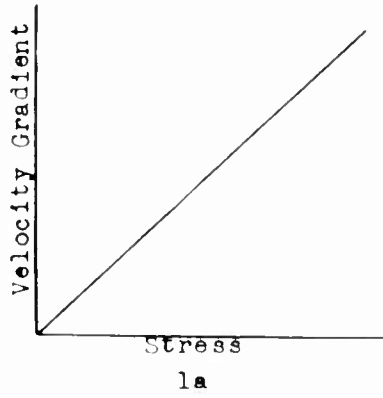
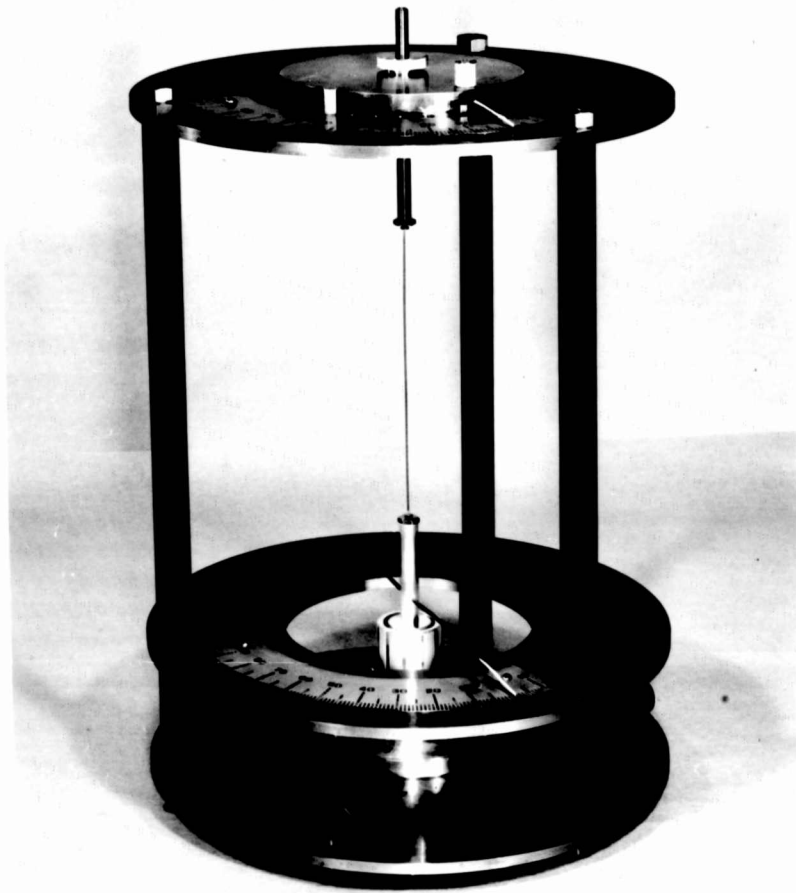
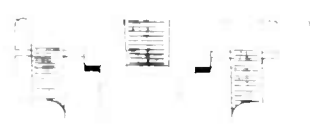
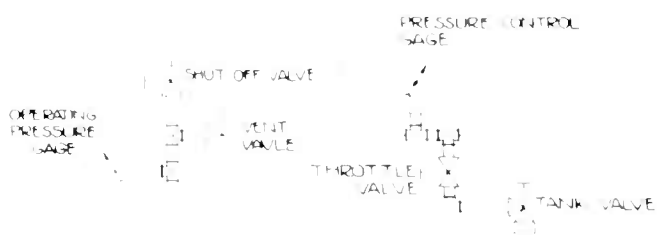


FIGURE 2





# CAPILLARY VISCOMETER



VISCOMETER CYLINDER

MAXIMUM STORAGE

CAPILLARY

BALANCE TANK

HIGH PRESSURE NITROGEN STORAGE TANK

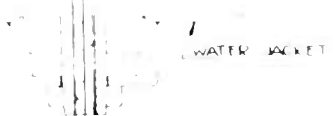
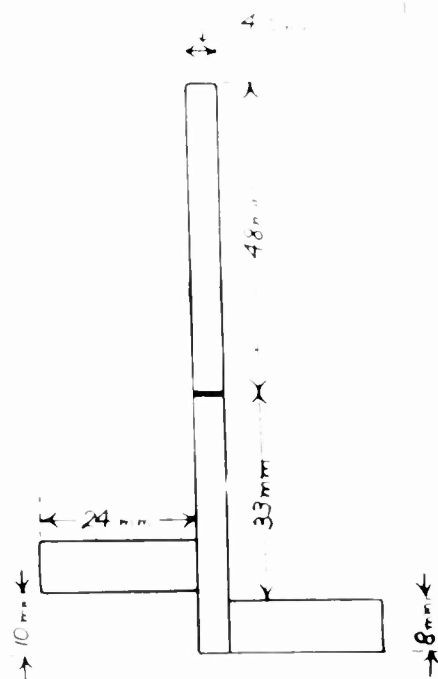
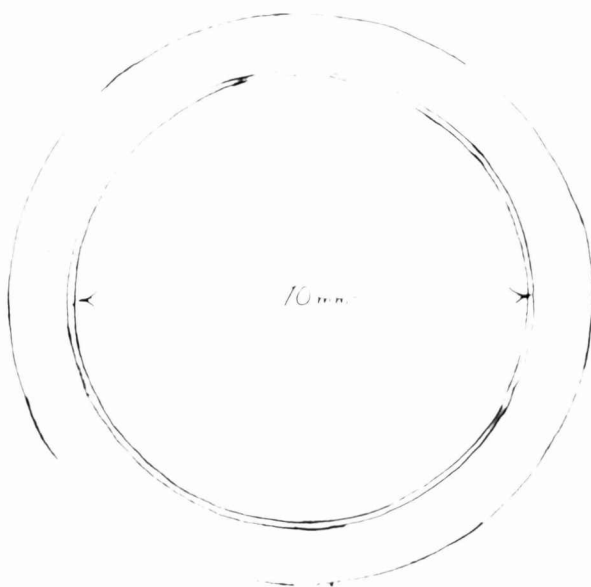
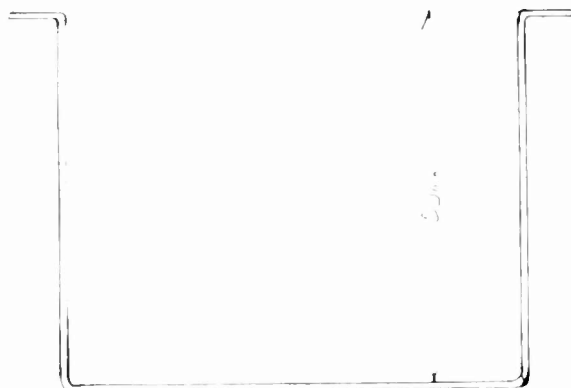


Figure 3

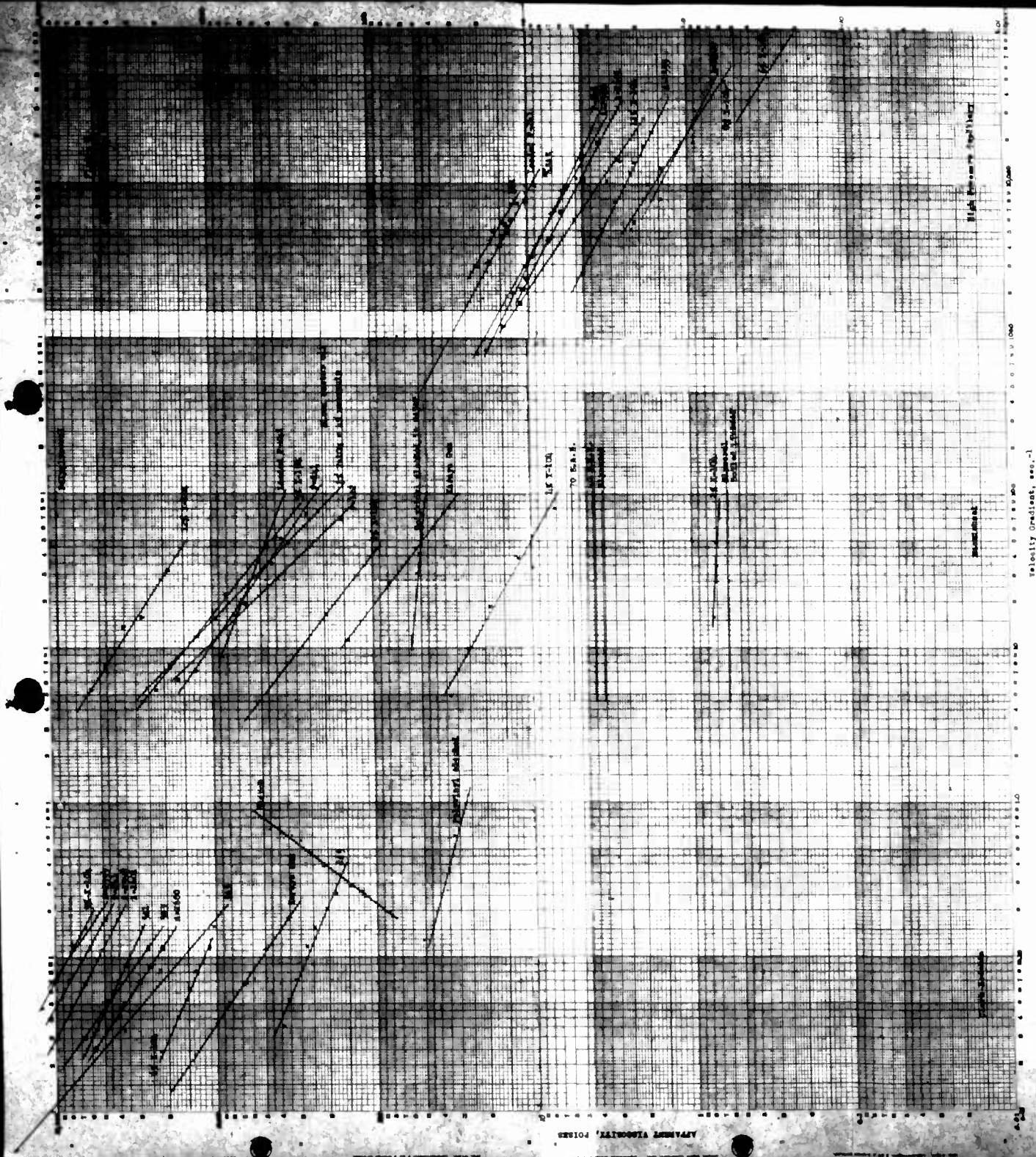
FIG. 4

FULL SCALE

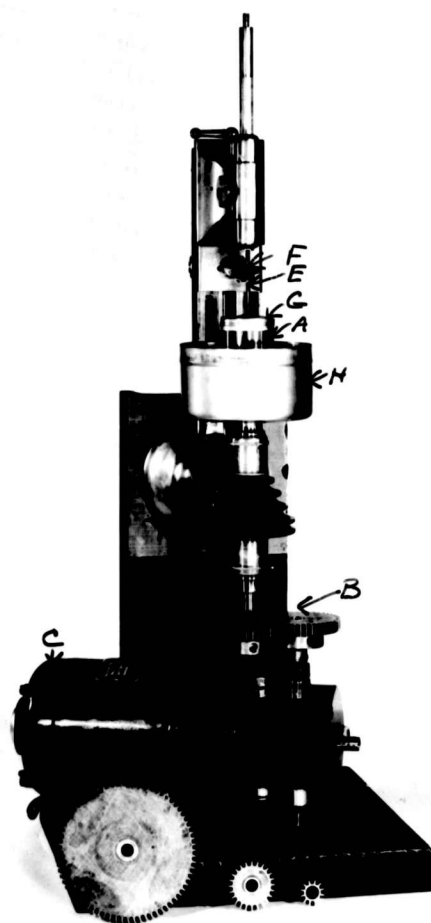


BLADE .015" THICK

OF BLADE 9 mm FROM CUP BOTTOM  
WHEN CORRECTLY POSITIONED.







# Figure 7.

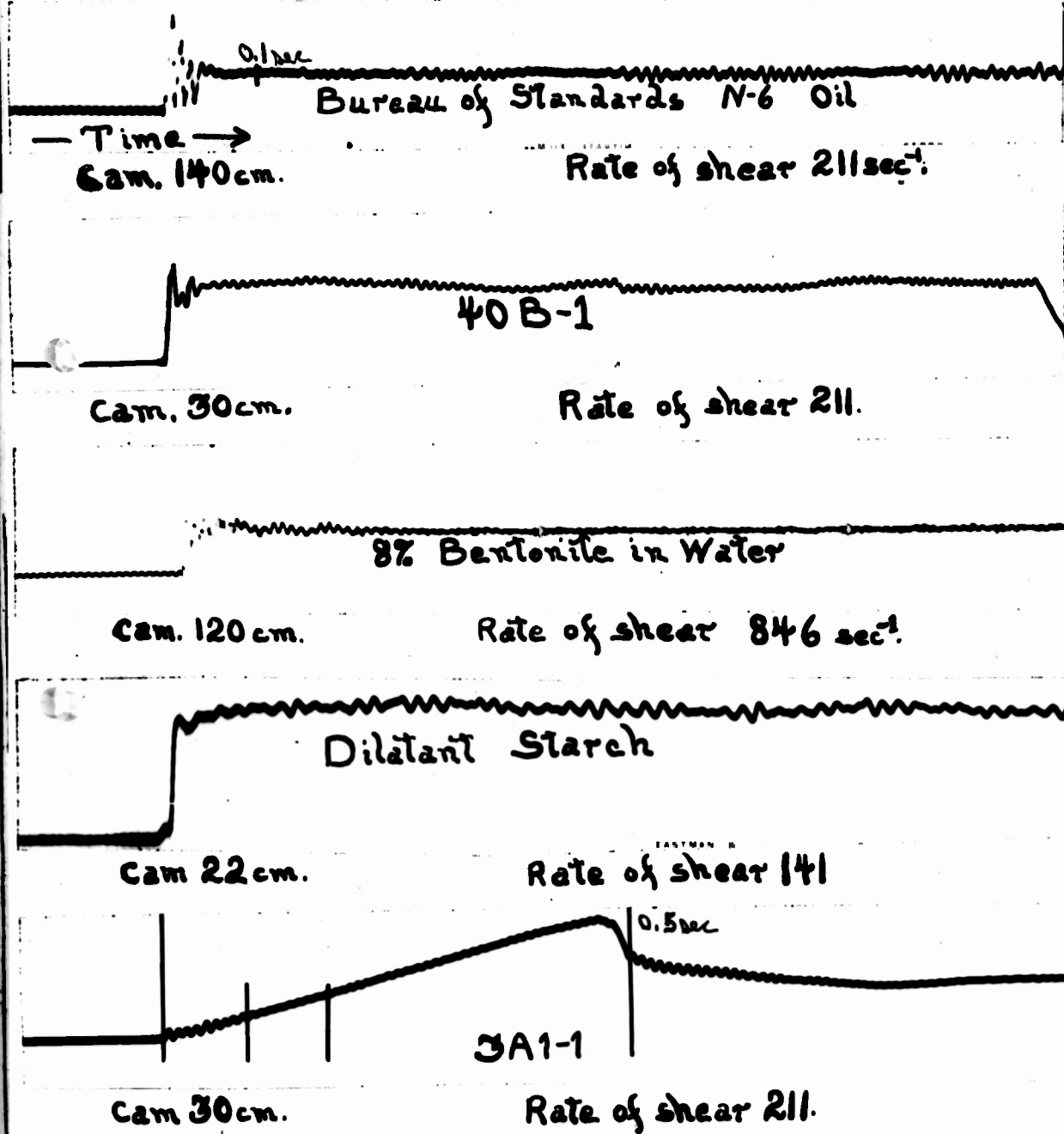
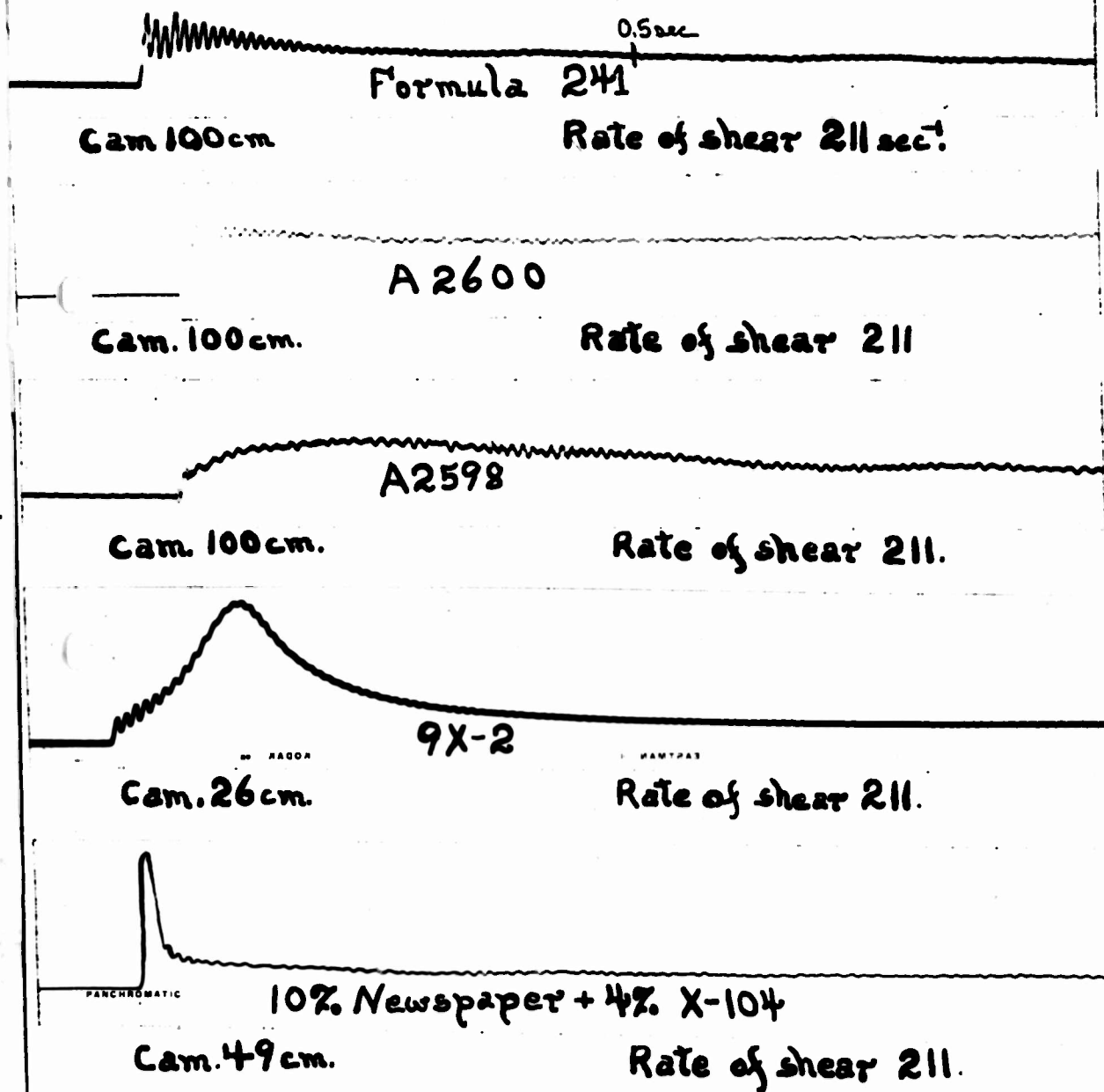
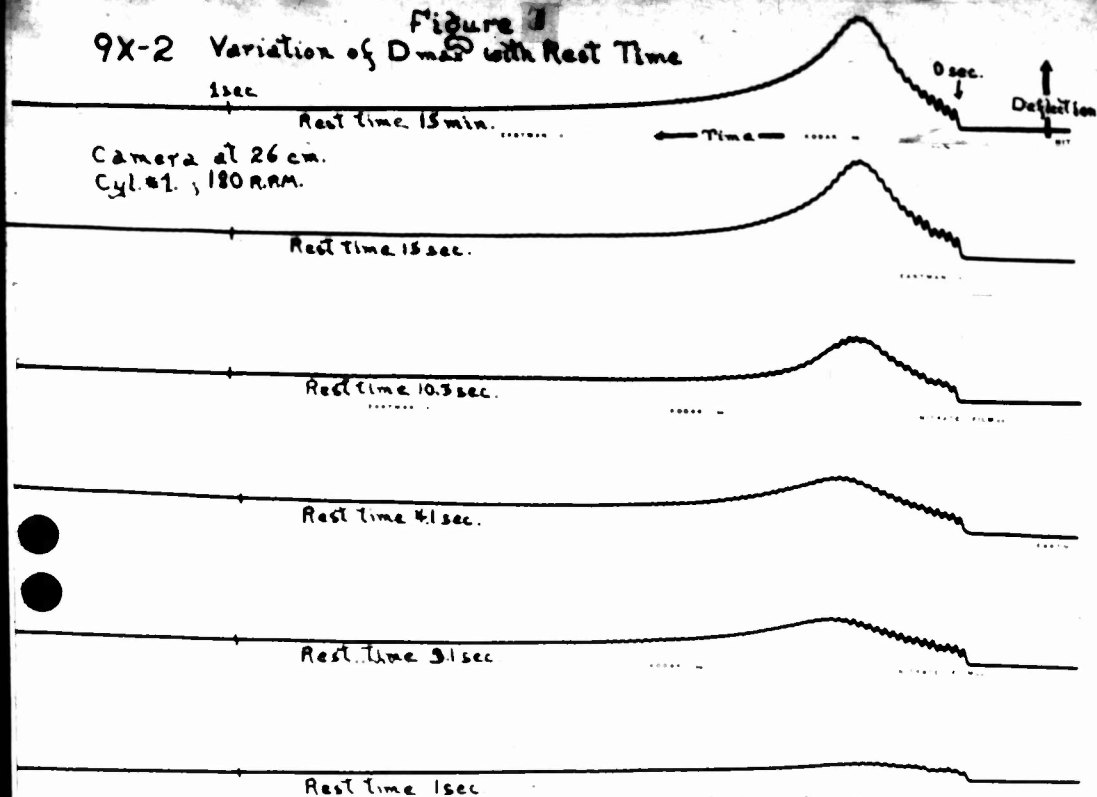


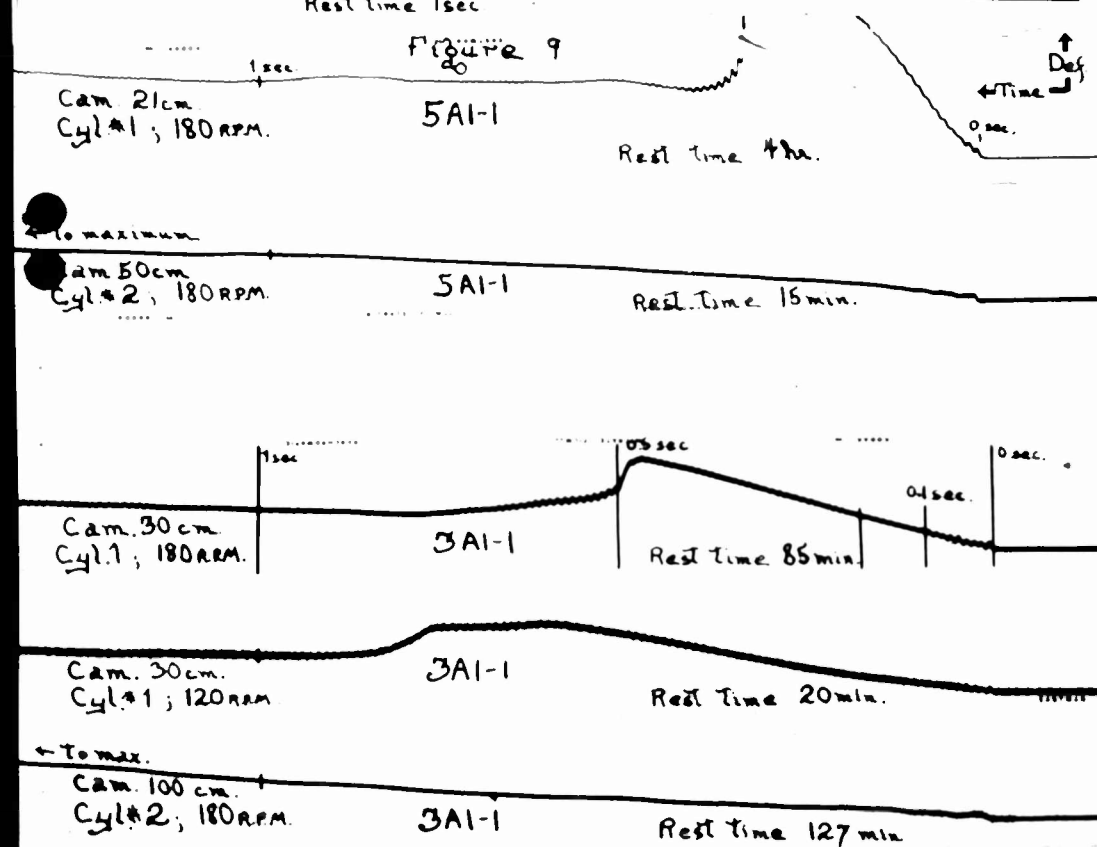
Fig. 7. (continued).



# 9X-2 Variation of $D_{max}$ with Rest Time



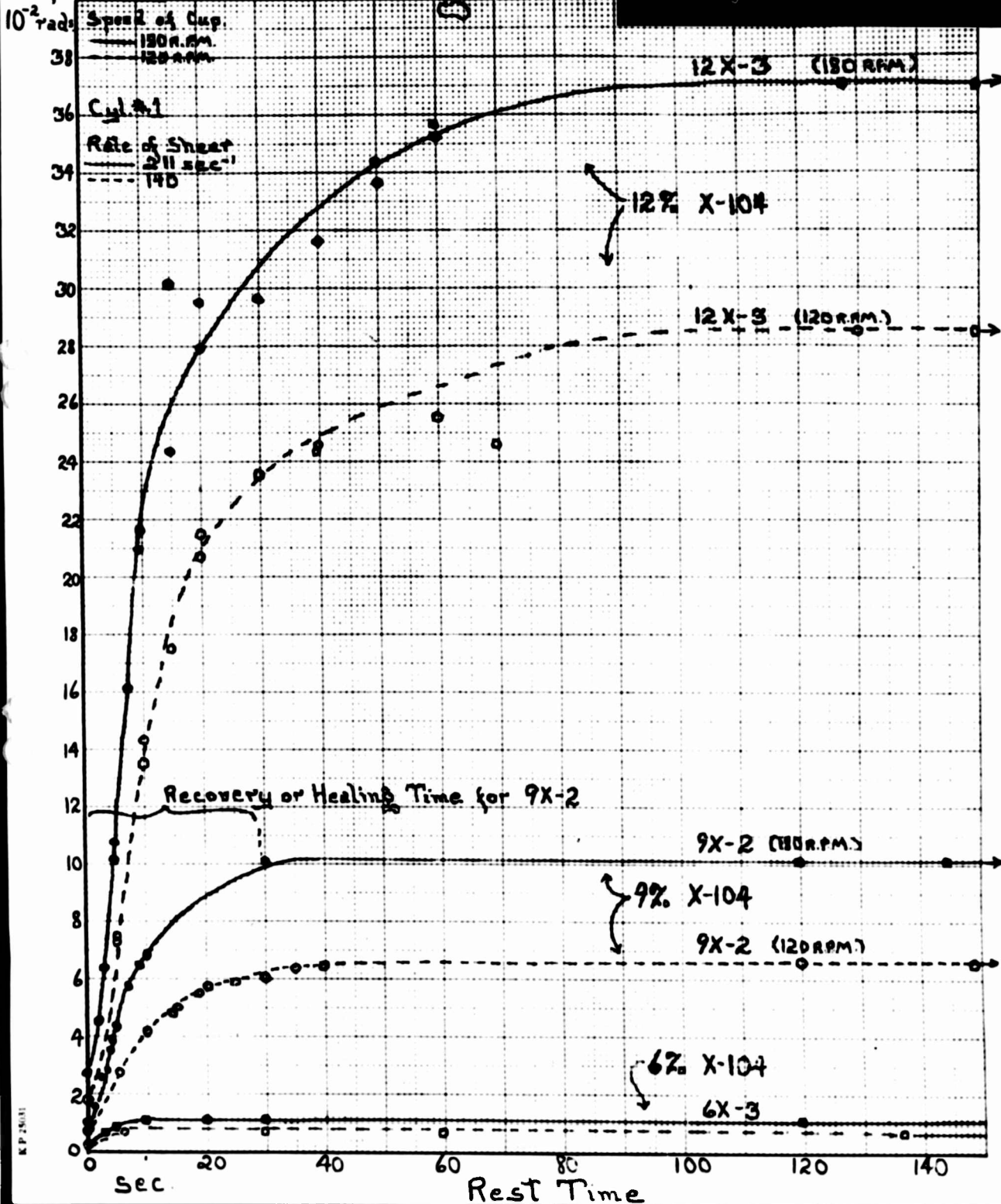
## FIGURE 9



-D<sub>max</sub>-  
Deflection

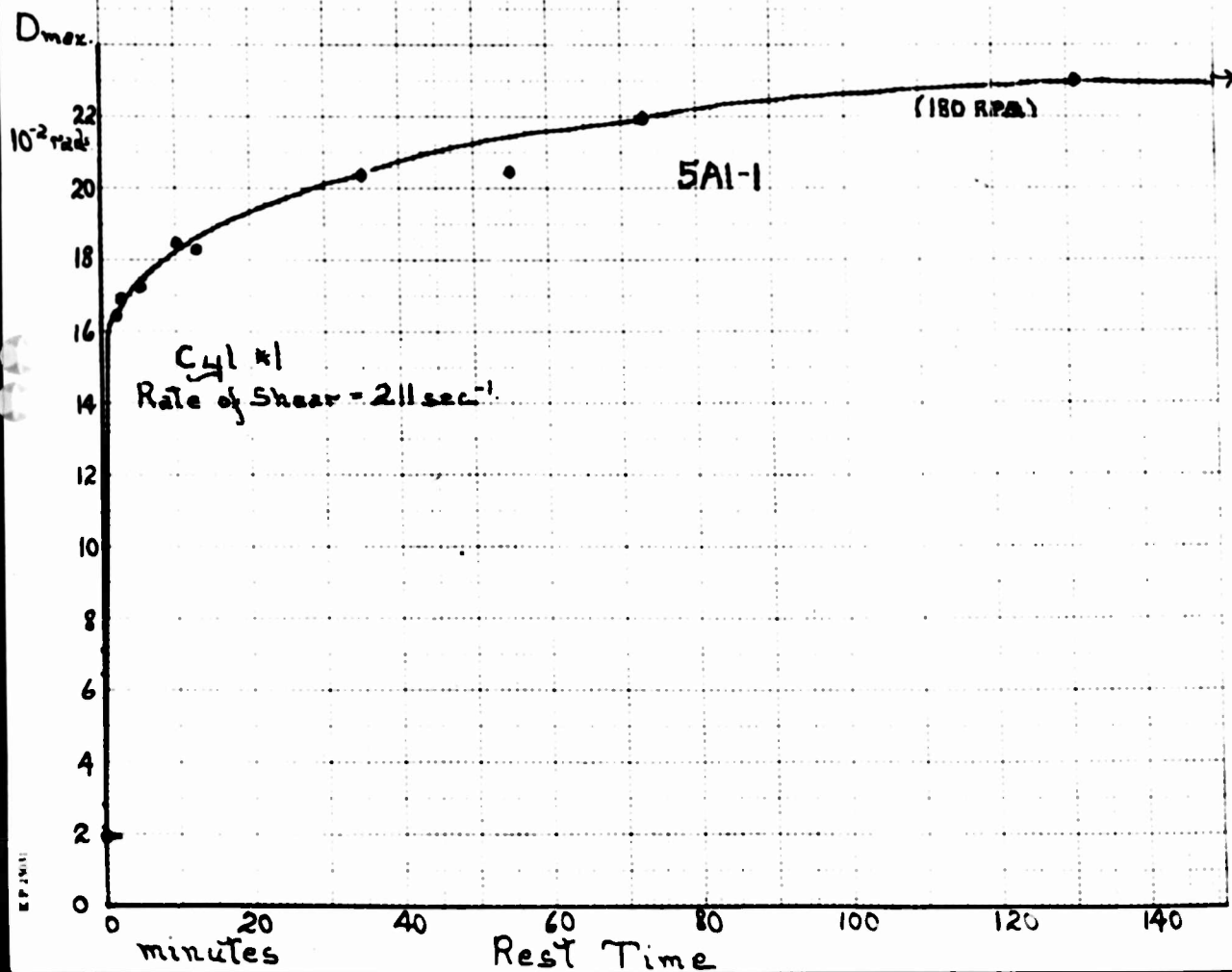
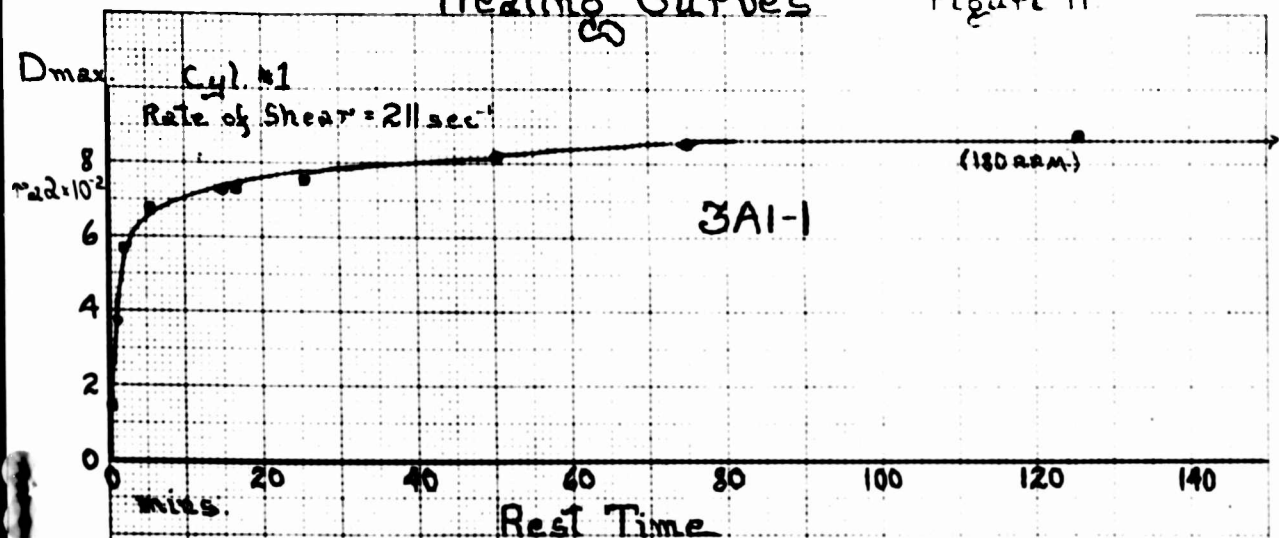
# Healing Curves

Figure 10



# Healing Curves

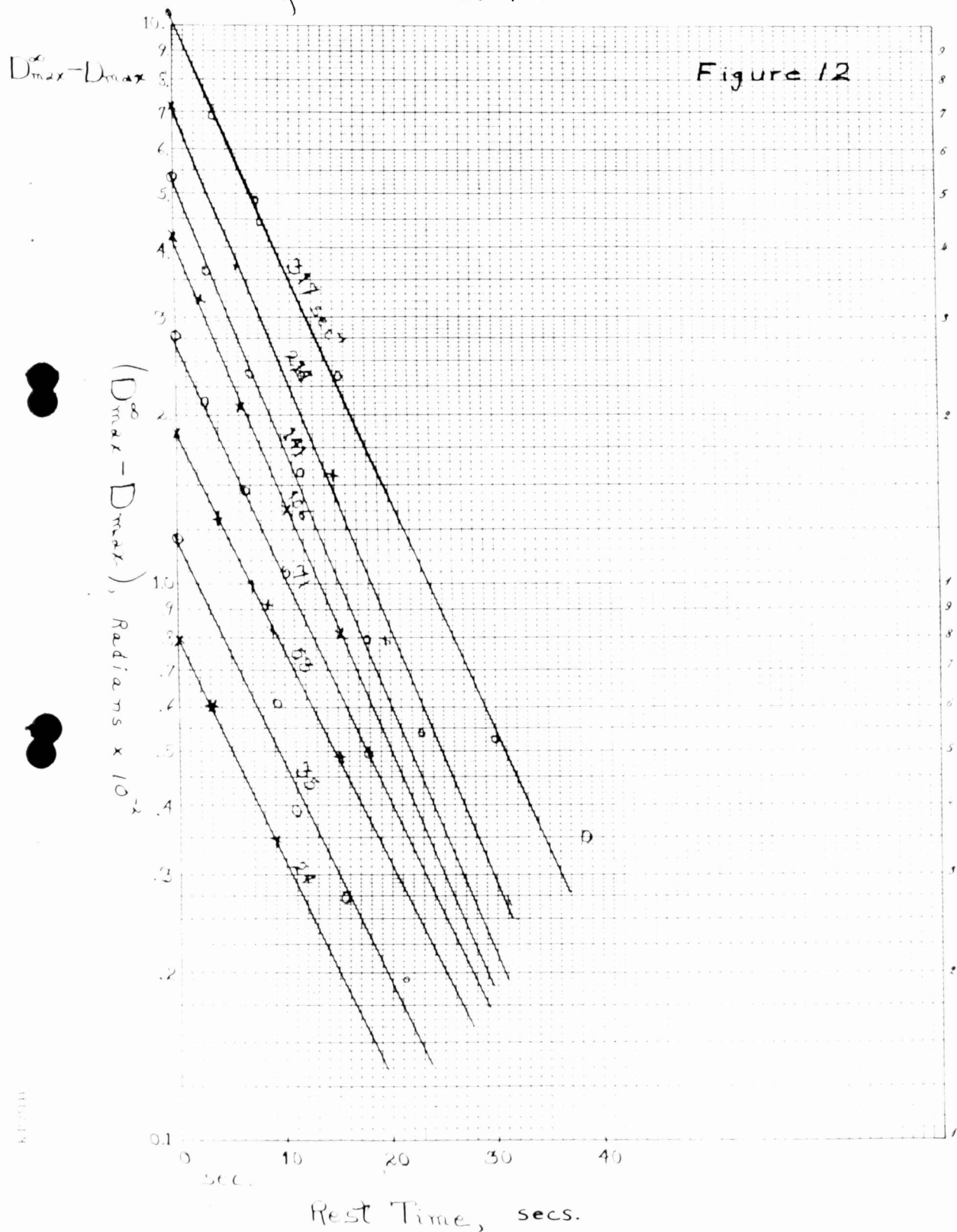
Figure 11





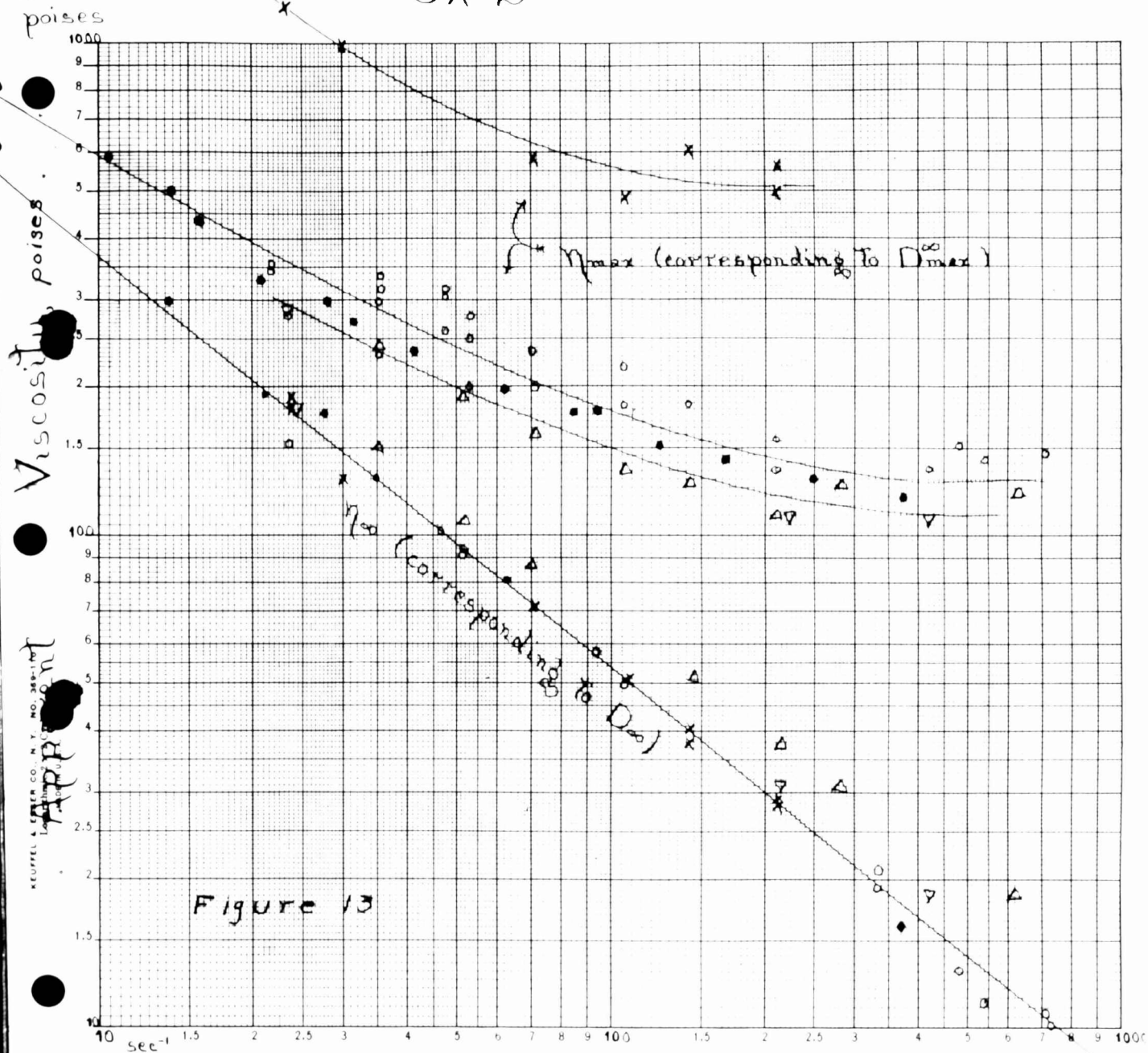
# Healing Curves at Various Rates of Shear for 9X-2 at 23°C.

Figure 12



# Variation of Apparent Viscosity with Rate of Shear and Temperature

— 9X-2 —



Apparent Rate of Shear at Inner Cylinder Wall, sec.<sup>-1</sup>

- |                 |                 |
|-----------------|-----------------|
| x Cyl 1 at 0°C  | ▽ Cyl 1 at 50°C |
| • Cyl 2 at 24°C | △ Cyl 1 at 70°C |
| ○ Cyl 1 " "     |                 |

8

7

6

5

4

3

2

1

0

0

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

19

20

21

22

23

24

25

26

27

28

Relaxation Curves

9% Napalm

0.016 in.

70°F

Figure 14

$\frac{dF}{dt}$

$F_{\infty}$

Ref:  
A-473 p.19  
6-12 RG

t in seconds

30

25

20

15

10

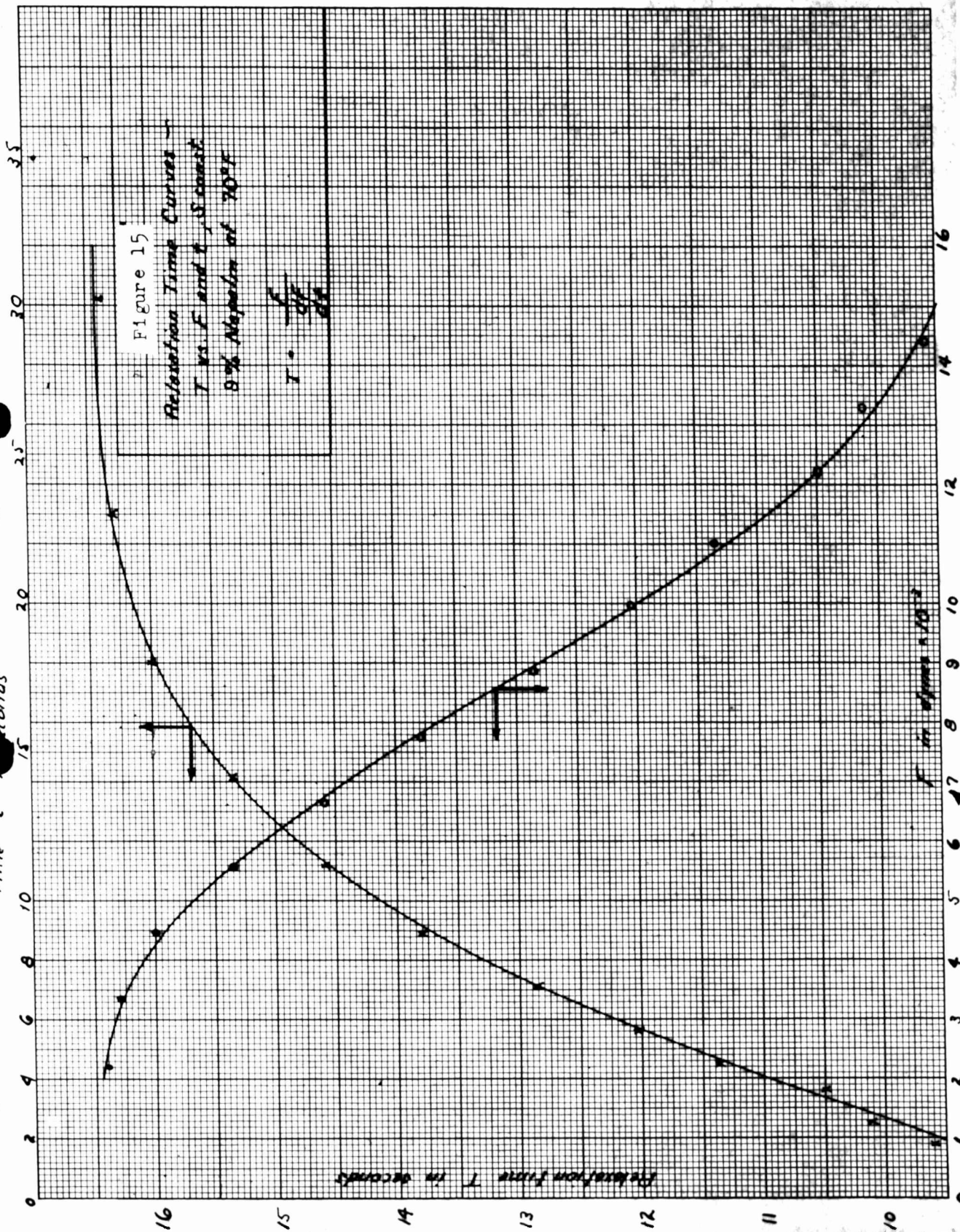
5

0





Time  $t$  seconds



$F$  in dynes  $\times 10^{-3}$



Time  $t$  seconds

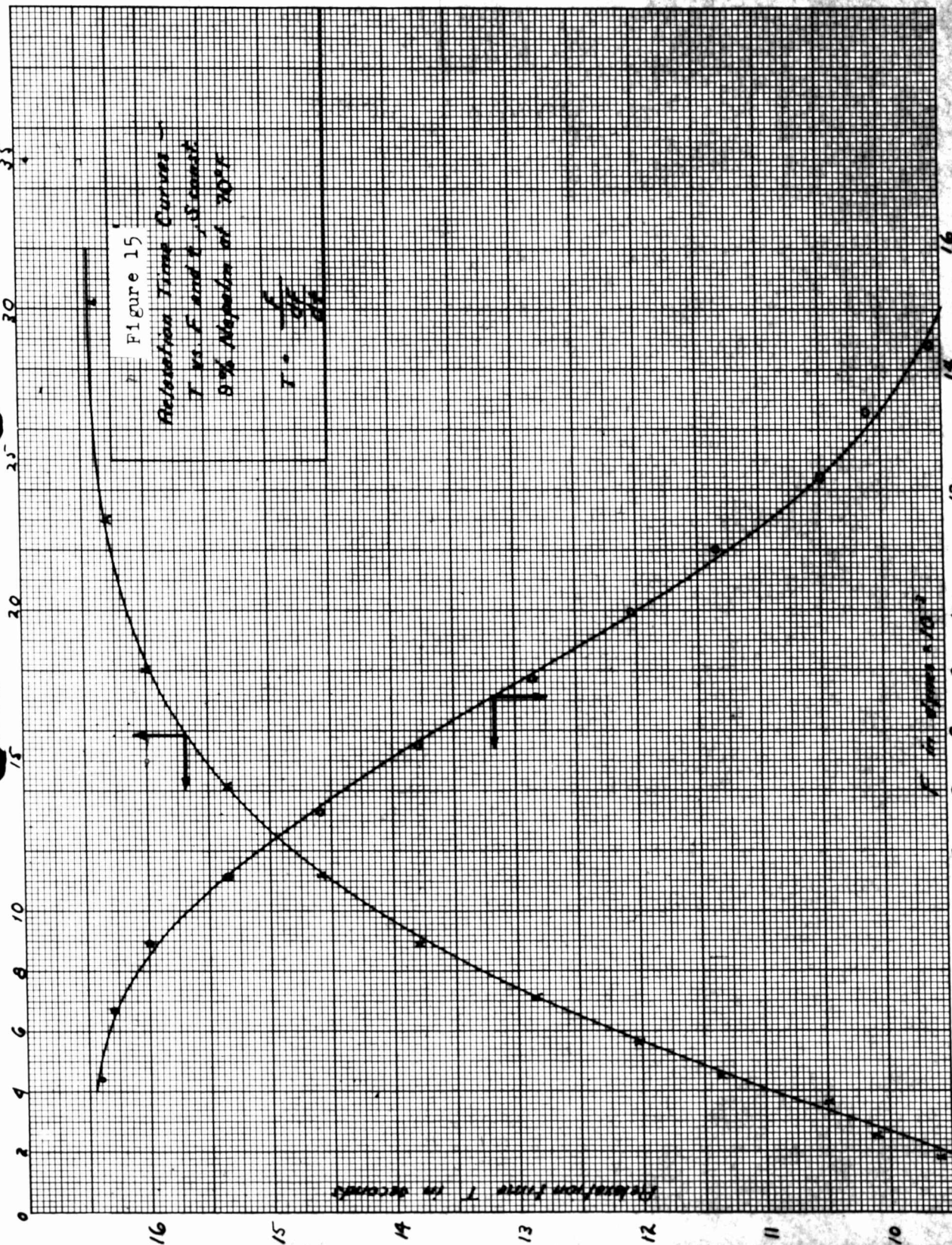
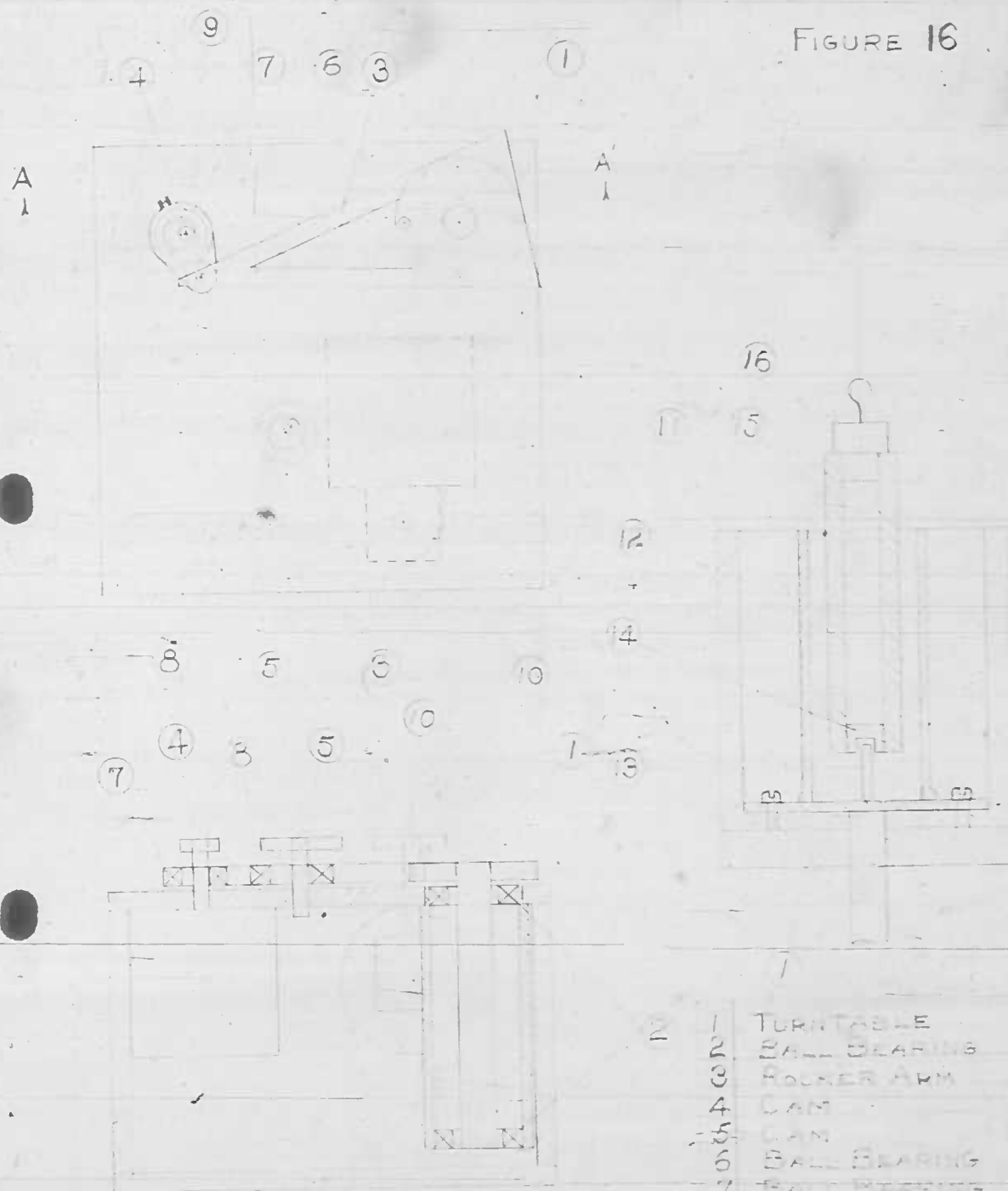


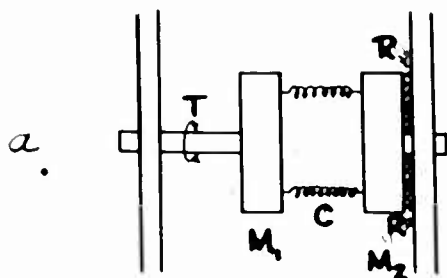
FIGURE 16



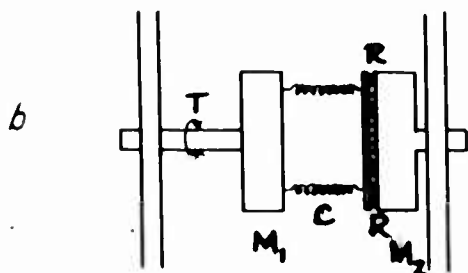
MOTOR 30-10 CAN BE USED GIVING  
SEVERAL ALTERNATIVE DRIVES OR  
MOTOR 30-10 CAN BE USED GIVING

- 1 TURNTABLE
- 2 BALL BEARING
- 3 CORNER ARM
- 4 CAN
- 5 CAN
- 6 BALL BEARING
- 7 BALL BEARING
- 8 BALL BEARING
- 9 MOTOR
- 10 MOTOR = REDUCER
- 11 THERMOSTATIC VALVE
- 12 OVER CENTER
- 13 GUIDE PIN
- 14 GUIDE HOLE
- 15 INNER CYLINDER
- 16 MIRROR

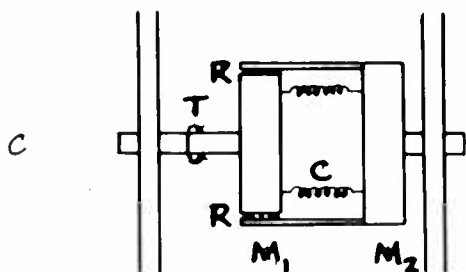




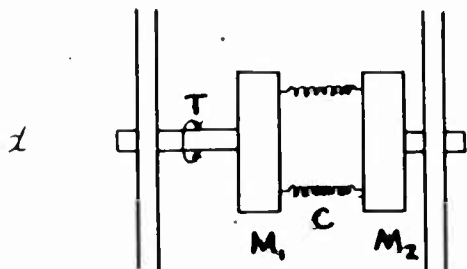
$$\frac{V_2}{V_1} = \frac{-j \frac{1}{\omega \sqrt{C M_2}}}{R \sqrt{\frac{C}{M_2}} + j \left( \omega \sqrt{C M_2} - \frac{1}{\omega \sqrt{C M_2}} \right)}$$



$$\frac{V_2}{V_1} = \frac{-j \frac{1}{\omega \sqrt{C M_2}}}{\frac{1}{R} \sqrt{\frac{M_2}{C}} + j \left( \omega \sqrt{C M_2} - \frac{1}{\omega \sqrt{C M_2}} \right)}$$



$$\frac{V_2}{V_1} = \frac{R \sqrt{\frac{C}{M_2}} - j \frac{1}{\omega \sqrt{C M_2}}}{R \sqrt{\frac{C}{M_2}} + j \left( \omega \sqrt{C M_2} - \frac{1}{\omega \sqrt{C M_2}} \right)}$$



$$\frac{V_2}{V_1} = \infty$$

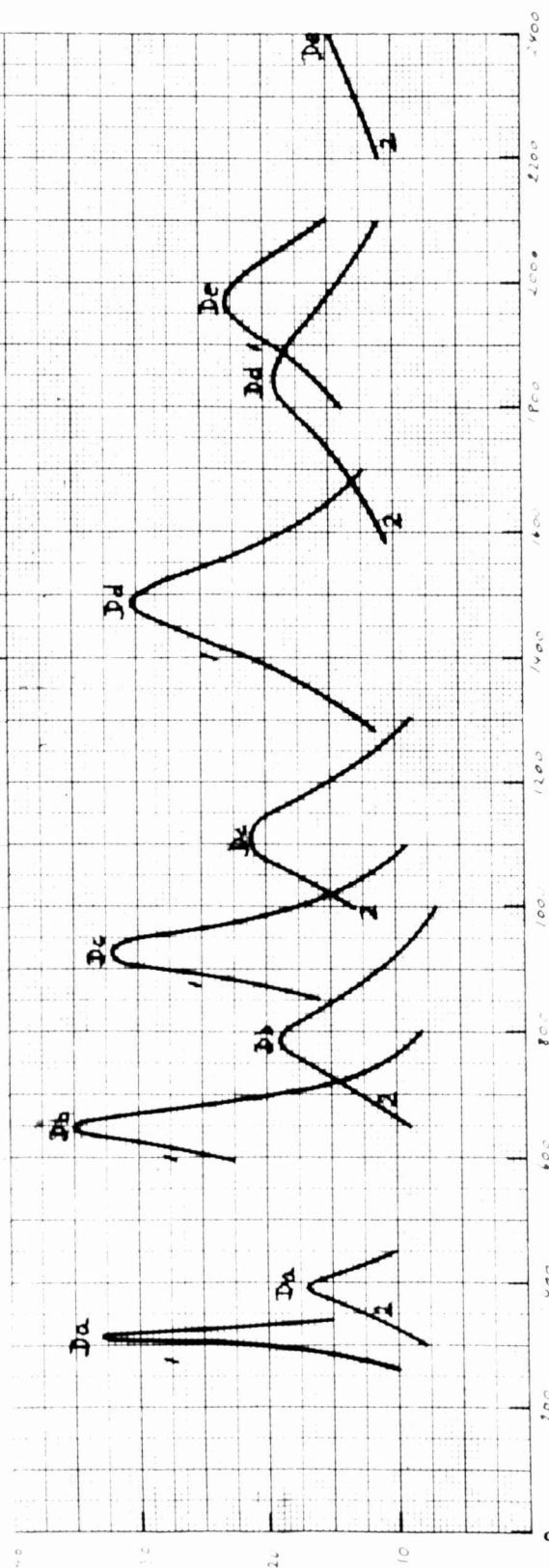
$$\omega_{\text{res}} = \frac{1}{\sqrt{C M_2}}$$

Fig. 17

Lettering refers to cylinders used

Symbol	Inside diam.	Length	Moment of inertia of liquid layer
D	outer cylinder	1.1 cm	5.0 cm
			3.4 grams cm <sup>2</sup>
	Outside diam.	Depth of immersion	Moment of inertia
a	inner cylinder	.79 cm	3.9 cm
b			11.9 grams cm <sup>2</sup>
c			2.7
d			1.6
e			.52
			25

1 liquid 8X4  
2 liquid 8X9

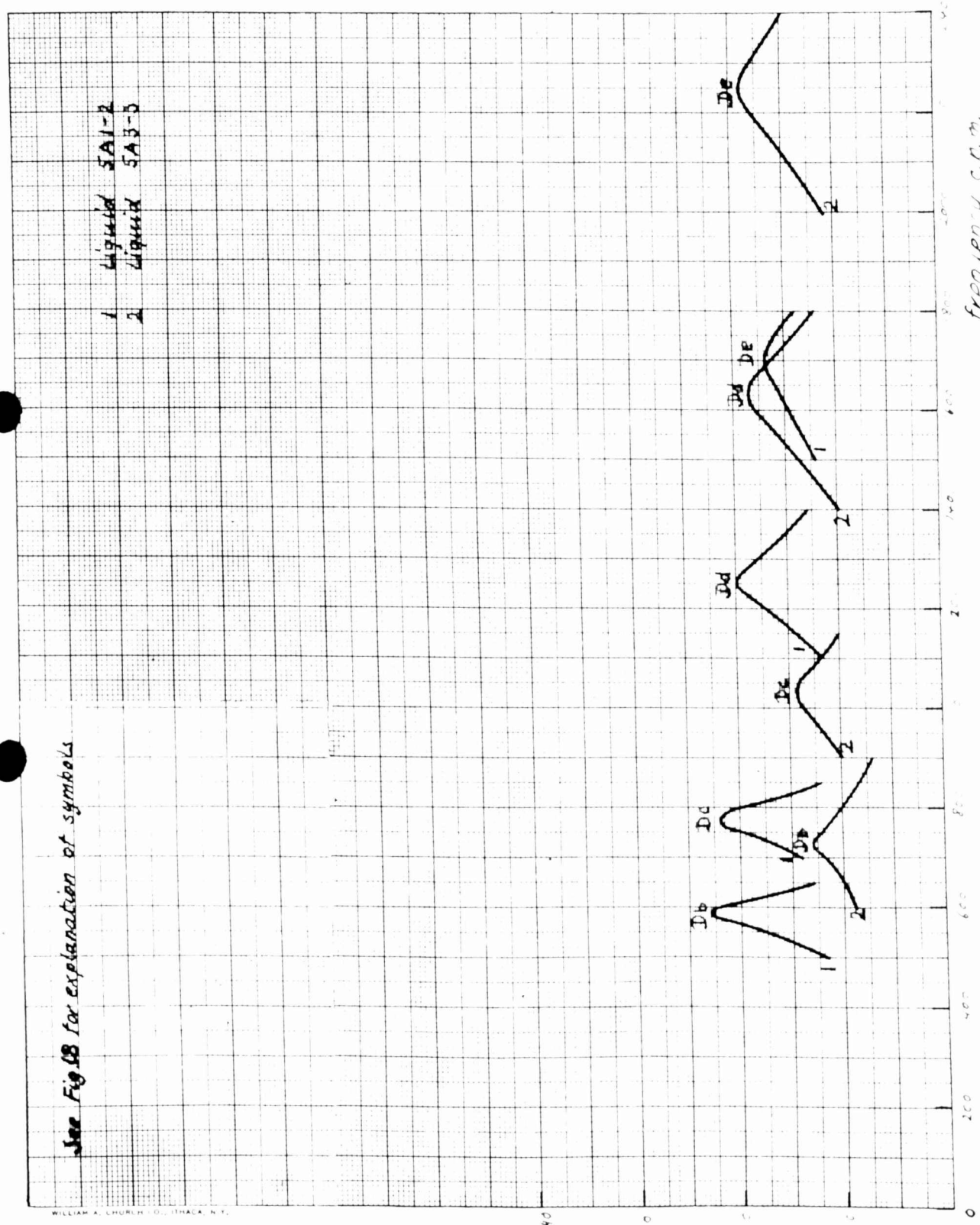


frequency c.p.m.

Figure 18

See Fig 18 for explanation of symbols

1 liquid 5A1-B  
2 liquid 5A3-B

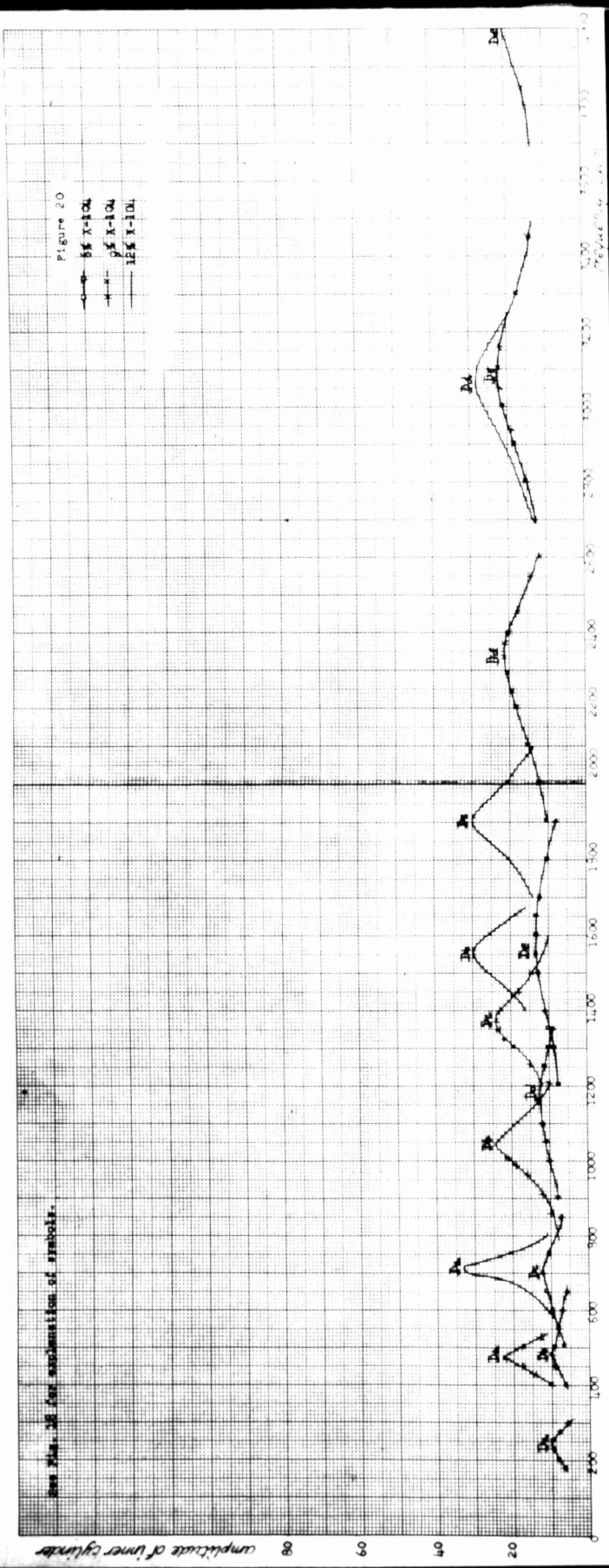


frequency c.p.m.

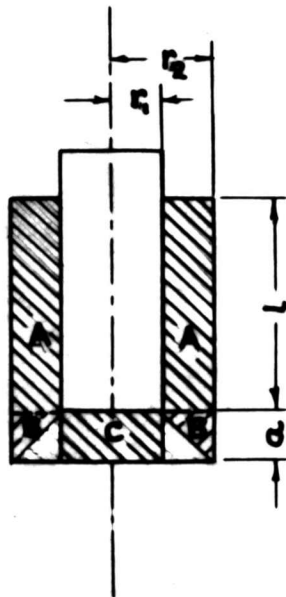
Figure 19

See Fig. 18 for explanation of symbols.

Figure 20



a



b

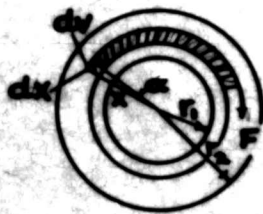


Figure 21



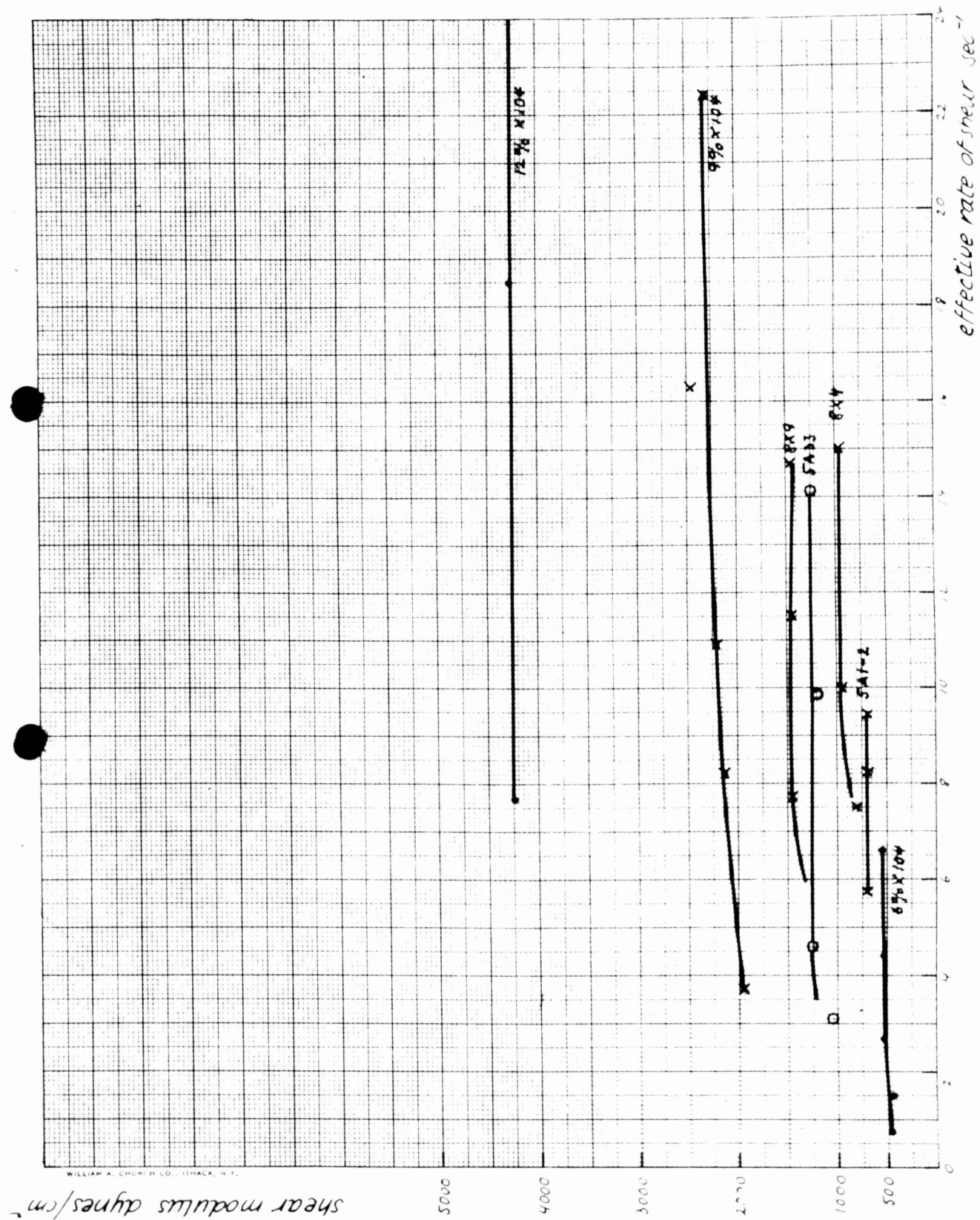
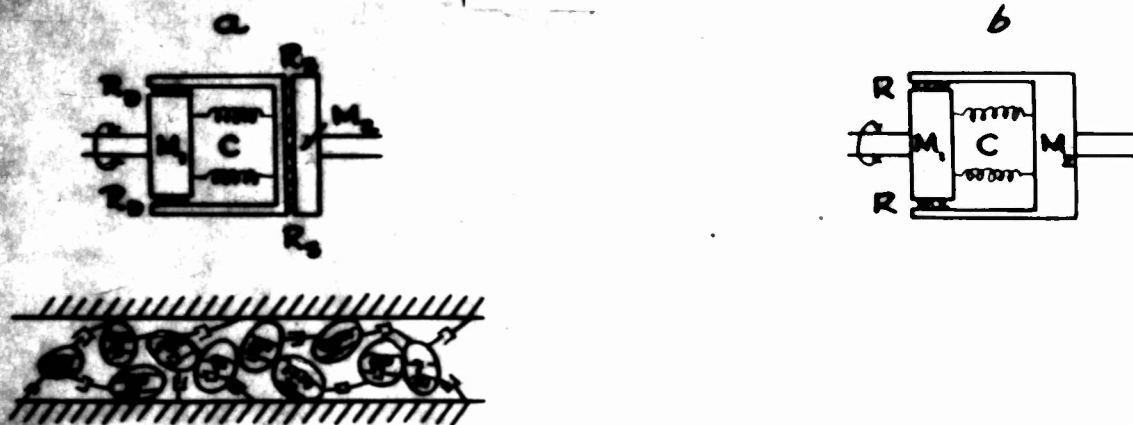


Figure 22



Figure 23



$$m = \frac{v_2}{v_1} = \frac{1 + j R_3 C \omega}{1 - \omega^2 C M_2 \left(1 + \frac{R_2}{R_3}\right) + j \omega C M_2 \left(R_3 \sqrt{\frac{R_2}{M_2}} + \frac{R_2}{R_3}\right)}$$

If  $\frac{M_2}{v_1} > 3$   $\omega_{res} \sim \frac{1}{\sqrt{C M_2}}$   
and  $\frac{v_2}{v_1}$  is simplified to

$$\left(\frac{v_2}{v_1}\right)_{max} \sim \frac{1 + j R_3 \sqrt{\frac{R_2}{M_2}}}{j \left(R_3 \sqrt{\frac{R_2}{M_2}} + \frac{R_2}{R_3}\right) - \frac{R_2}{R_3}}$$

It was found that for all liquids measured so far

$$R_3 \gg R_2 \text{ and } R_3 \sqrt{\frac{R_2}{M_2}} \ll 1$$

Therefore

$$\left(\frac{v_2}{v_1}\right)_{max} \sim \frac{1}{R_3 \sqrt{\frac{R_2}{M_2}} + \frac{1}{R_3} \sqrt{\frac{M_2}{C}}}$$

$$R_3 \sim \frac{\sqrt{\frac{M_2}{C}}}{\left(\frac{v_2}{v_1}\right)_{max}} - \frac{M_2}{C R_3}$$

with the experimental apparatus of Fig. 1

$$R_3 = \frac{1}{4\pi\ell} \left(\frac{1}{r_1^2} - \frac{1}{r_2^2}\right) R_2 \text{ poises}$$

for the D cylinder

$$R_3 = 6.45 \cdot 10^{-2} R_2 \text{ poises}$$

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LAWRENCE, KANSAS  
MADE IN U.S.A.

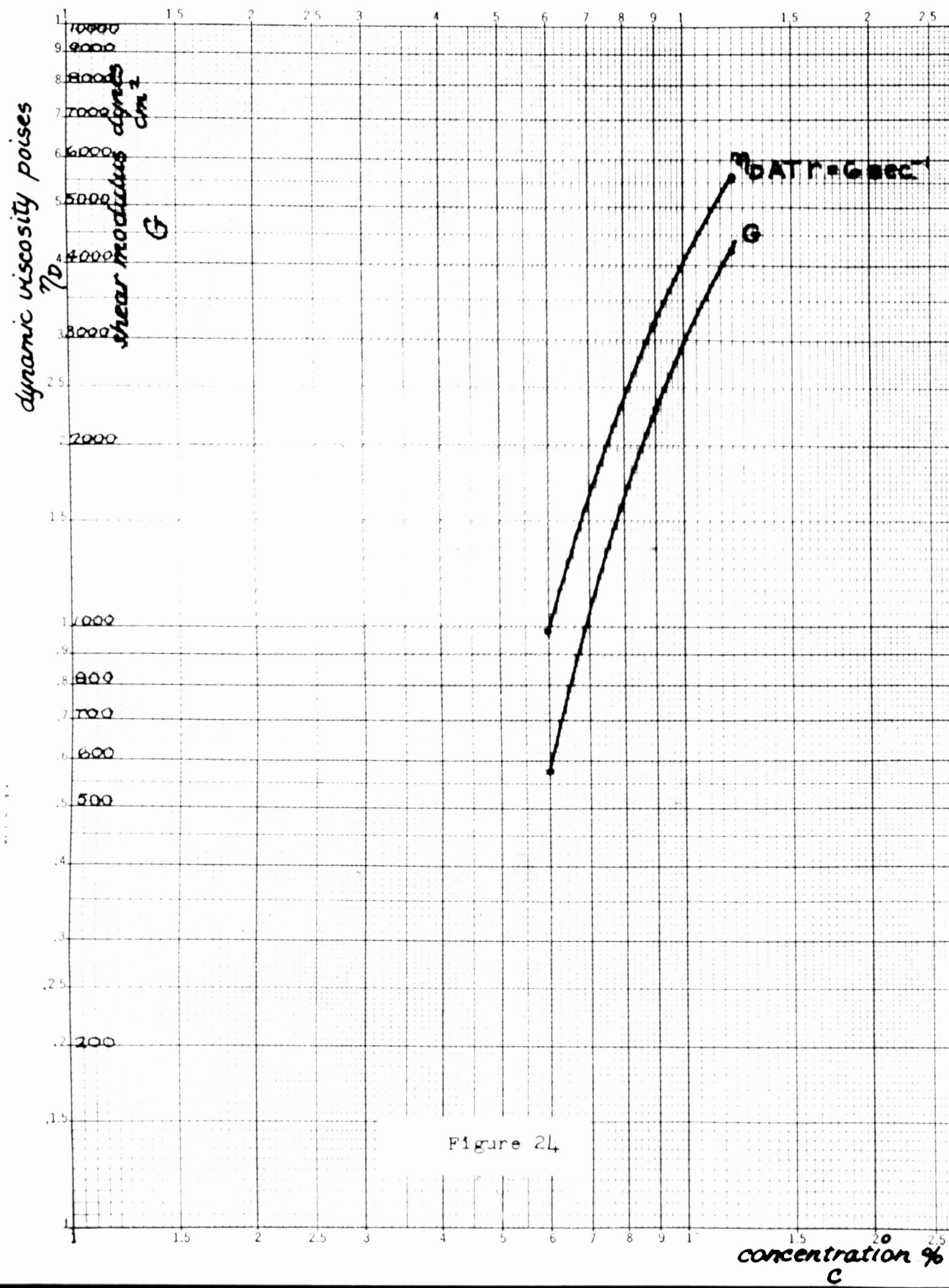
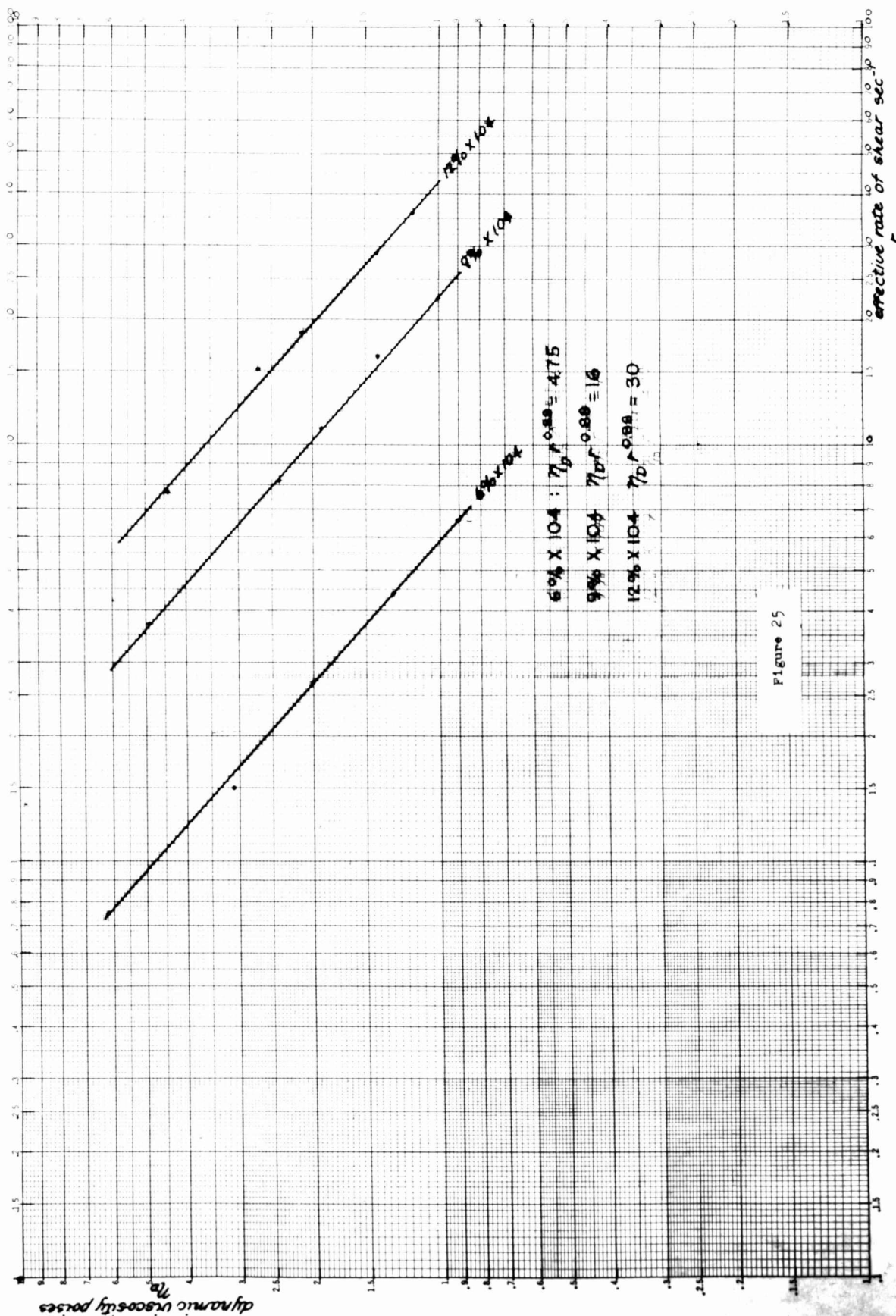
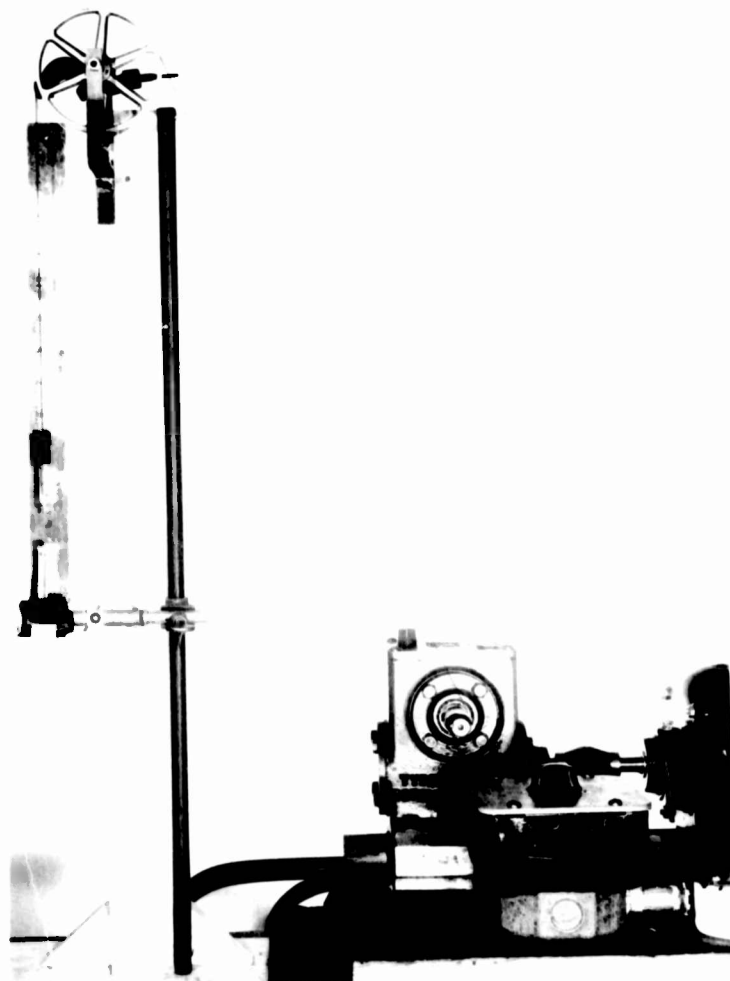
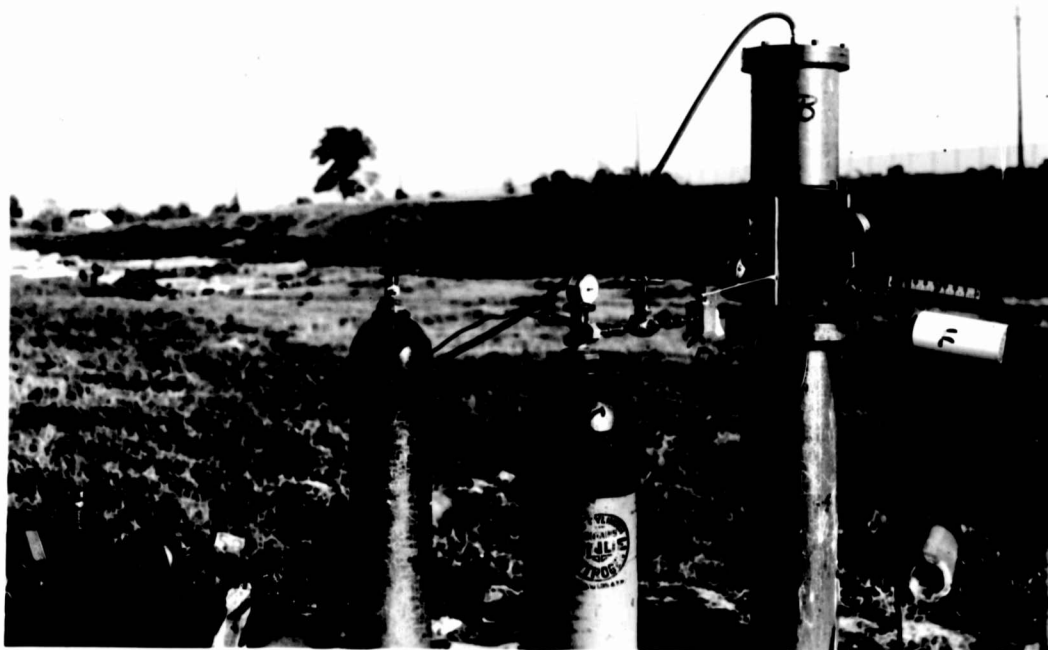


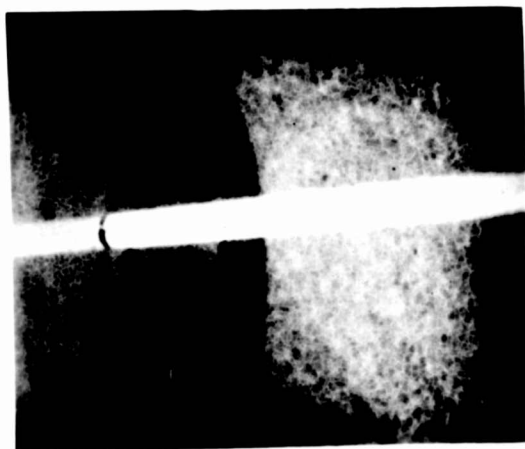
Figure 24

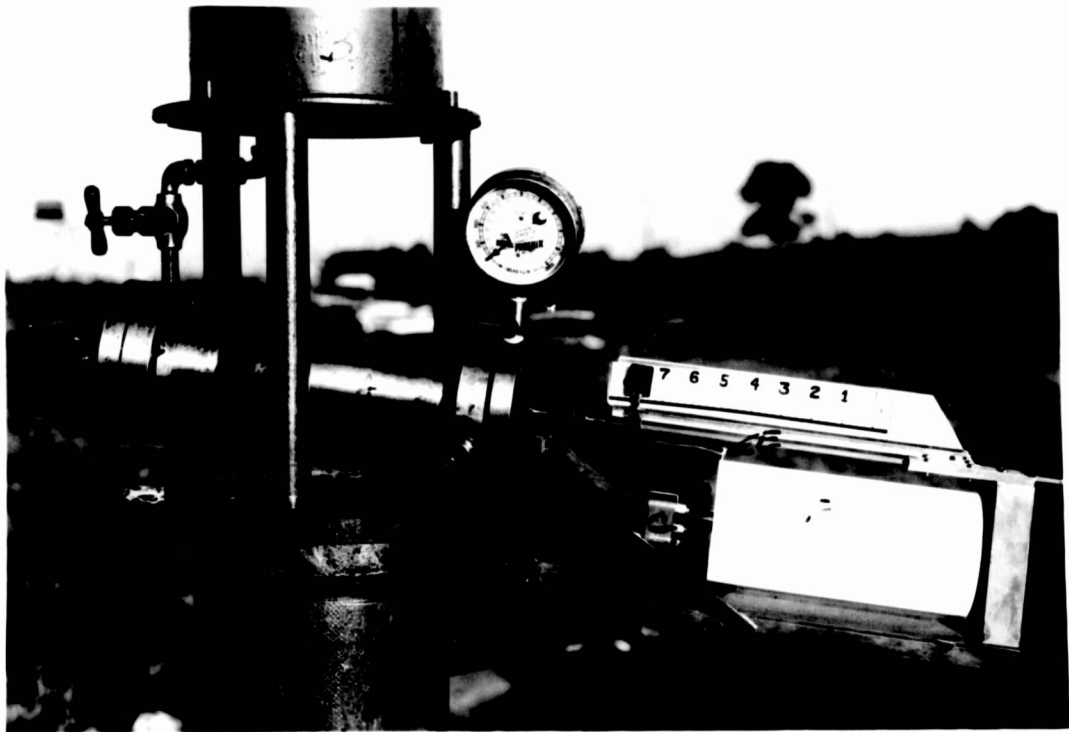






27a







100 percent polymer

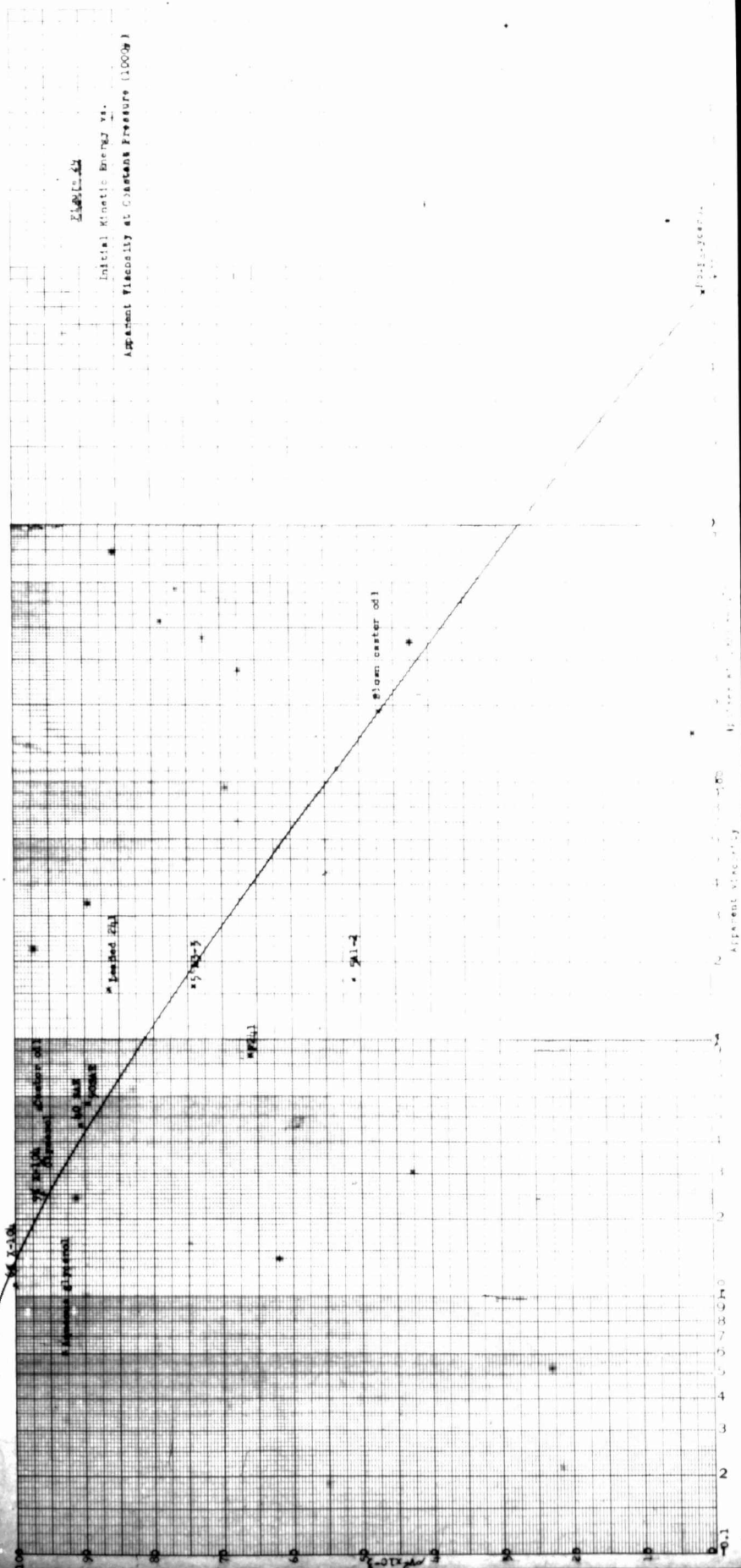
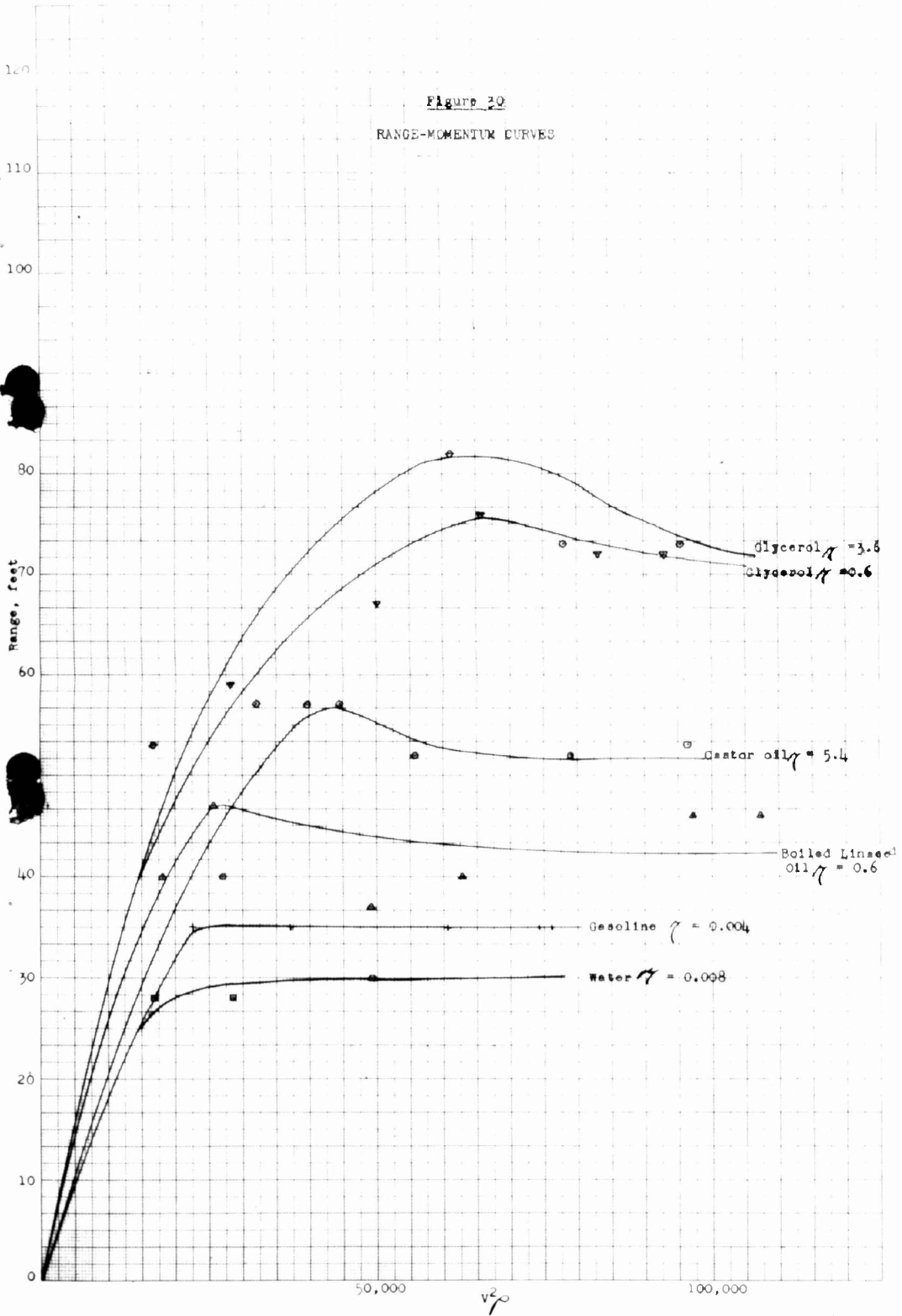




Figure 20  
RANGE-MOMENTUM CURVES



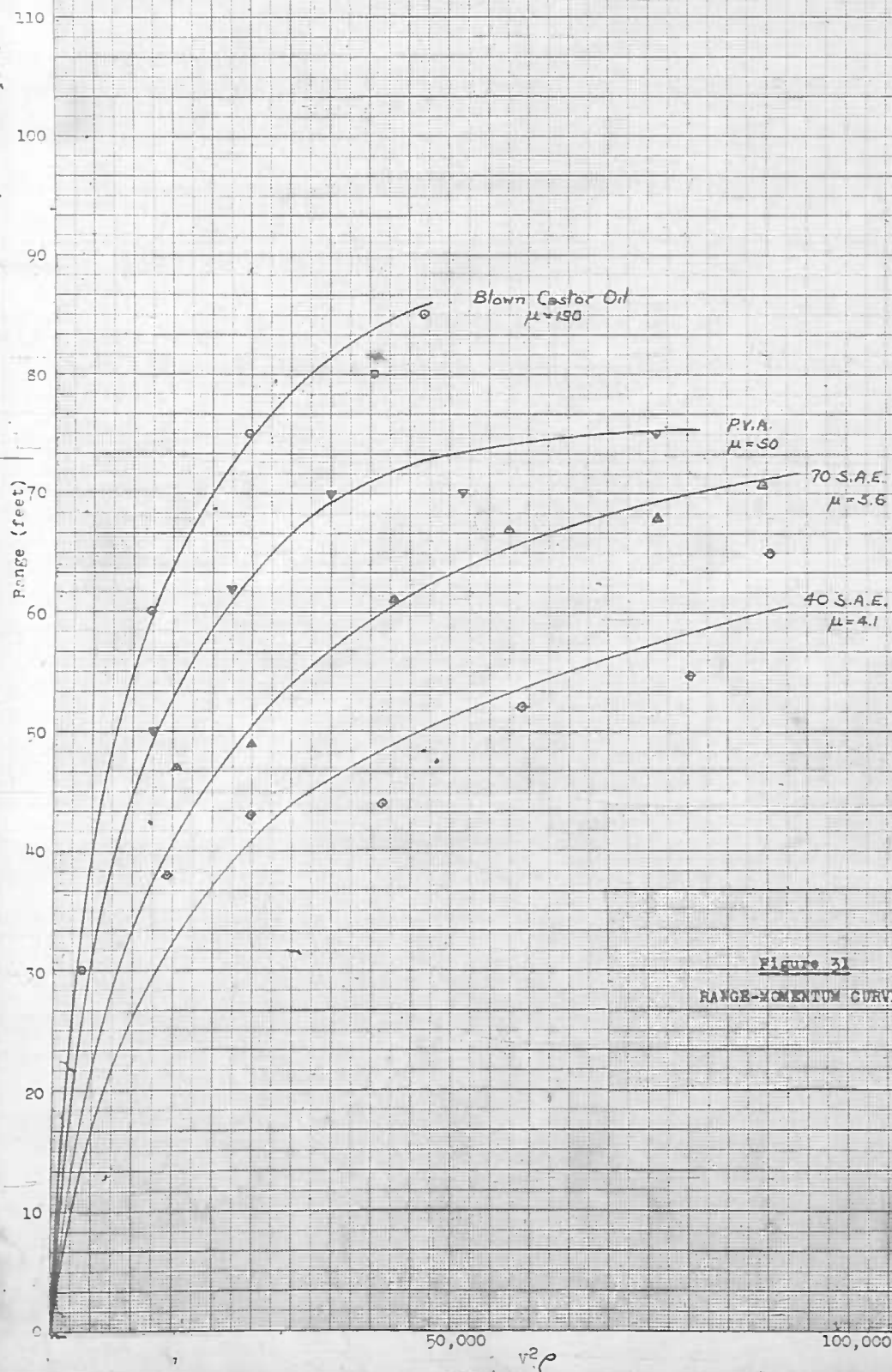
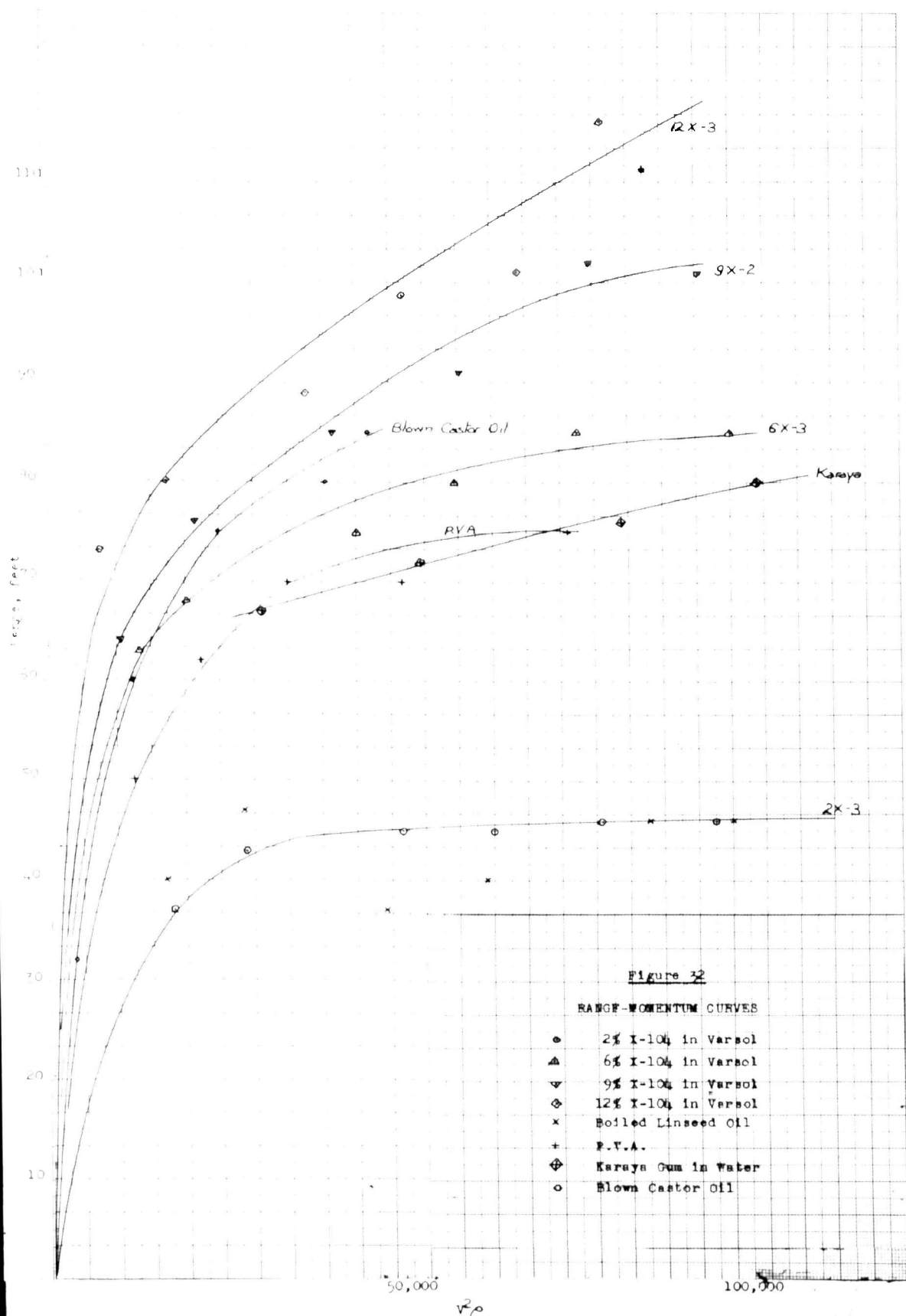
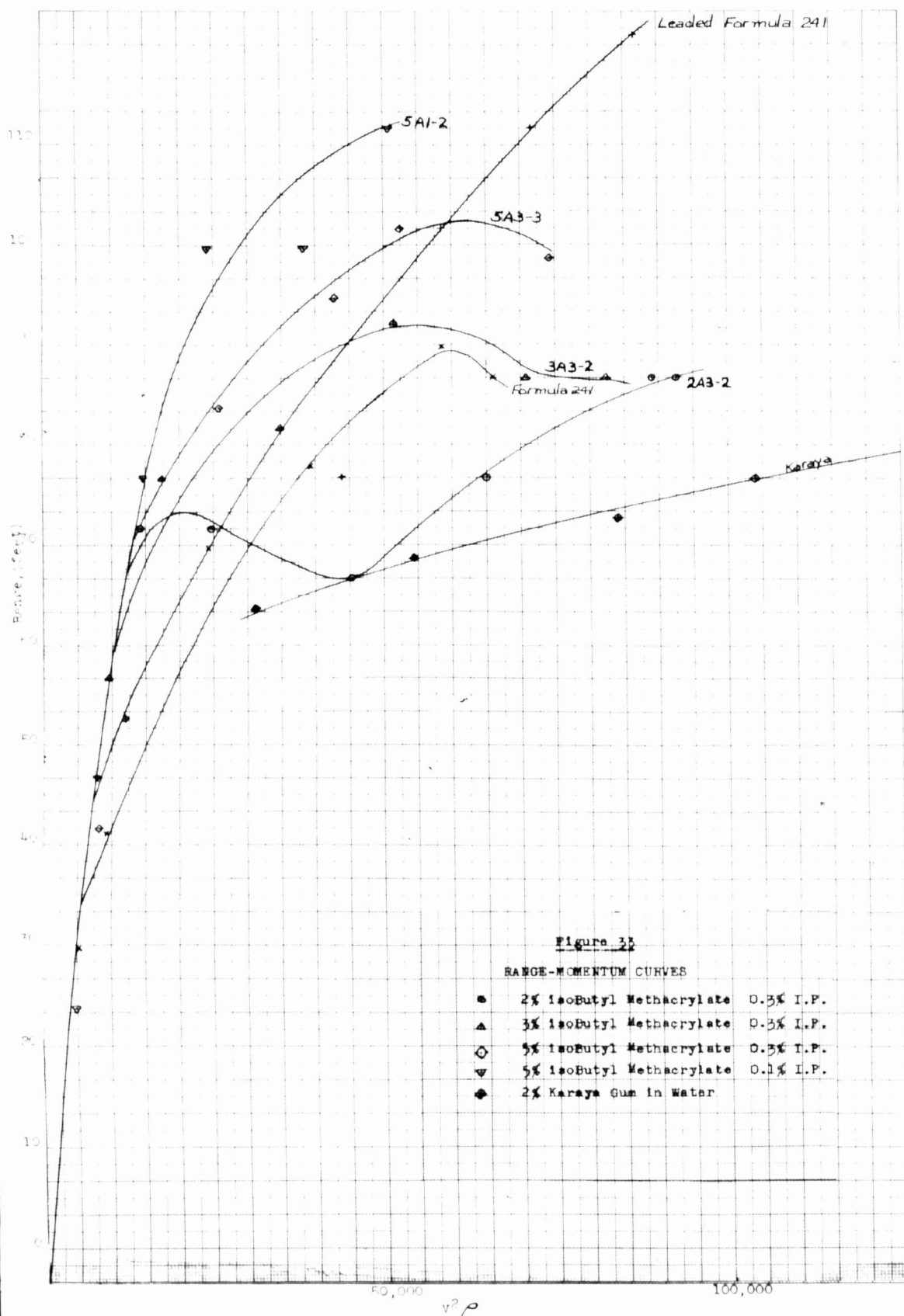
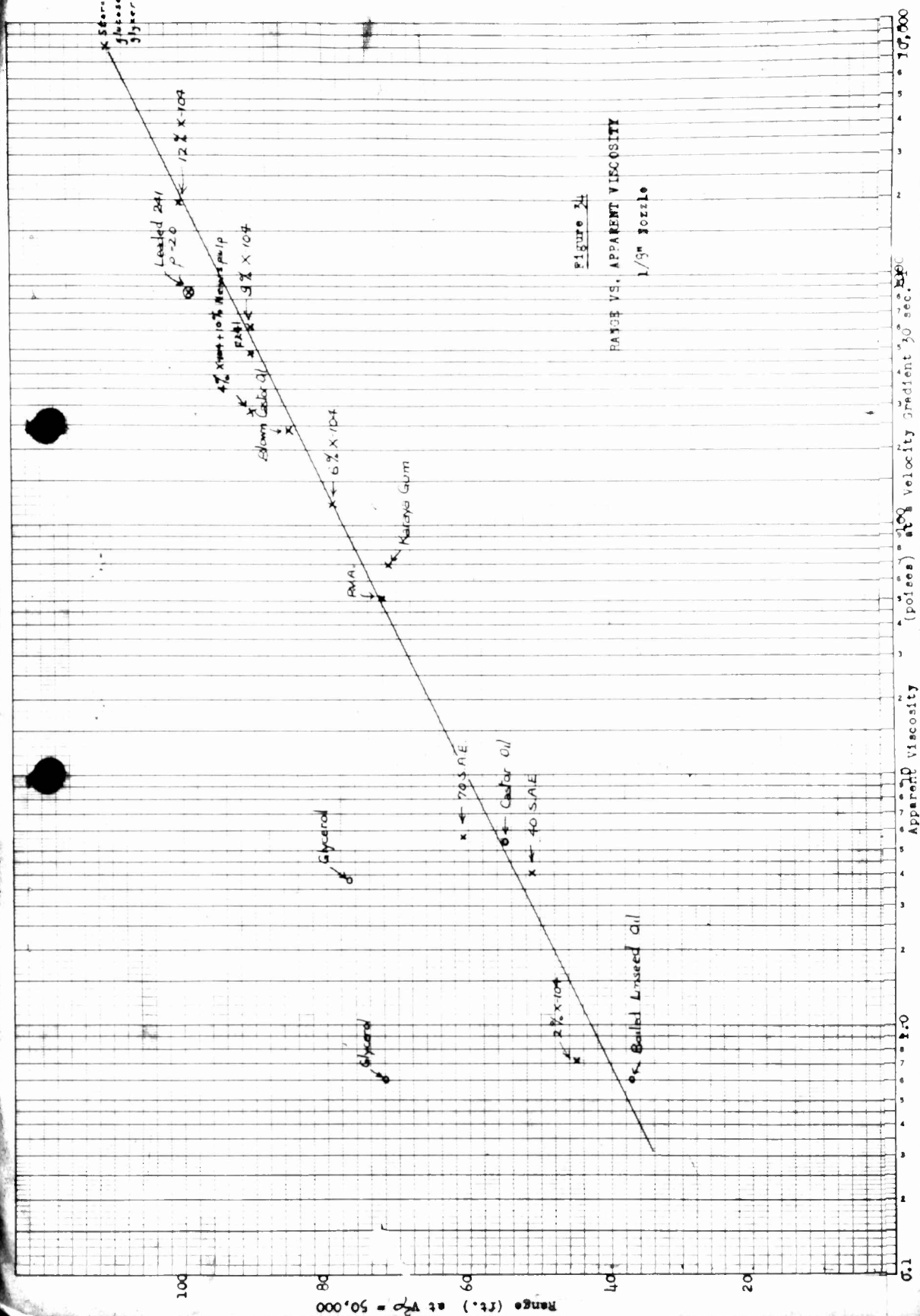


Figure 31  
RANGE-MOMENTUM CURVES









REEL - C

1 3 5 8

A.T.I.

3 3 5 7 6

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TITLE: Rheological Properties of Thickened Liquids

AUTHOR(S): Carver, E. K.; Broughton, G.

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ABSTRACT:

In order to improve the performance of flame thrower fuels, the rheological properties of thickened liquids were investigated. The fluids were of two main types: solutions of a basic aluminum soap in gasoline, and methacrylate copolymers also dissolved in gasoline, with or without the addition of a soap such as sodium stearate. The prime requirements for a flame thrower thickened fluid is pseudoplasticity. Measurements of the apparent viscosity, modulus of rigidity, work hardening, thixotropy and other properties of a large number of thickened fluids were made using a variety of instruments. Measurements were made with the normal viscosimetric techniques, at frequencies of from 5 to 600 cps and under suddenly imposed shock. A limited number of practical tests were made and for unignited flame thrower studies a 1/8" 37° conical nozzle was installed. A number of M56 incendiary bombs were filled with widely varying liquids and the results on static ignition studied.

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